STUDIES ON THE SYNTHETIC INORGANIC ION EXCHANGERS BASED ON HETEROPOLY ACIDS AND THEIR SALTS

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CERTIFICATE

This is to certify that the work described in this thesis is the original work of my research scholar, Mr. Haseem Ahmad Shakeel and it is suitable for submission for the award of Ph.D. degree in Chemistry of the Aligarh Muslim University, Aligarh, India.

(Mohsin Qureshi)
SUPERVISOR

IN THE GOOD NAME OF ALLAH PAK,
THE MOST BENEFICENT AND MERCIFUL

[redacted]

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LIST OF PUBLICATIONS

(Papers communicated)

1. Synthesis and Ion Exchange Properties of thermally stable and Thorium(IV) selective Tin(IV) molybdosilicate : Comparison with other Tin(IV) based ion exchangers (Reactive Polymers, U.S.A.).

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2. Separation of certain organic pollutants containing tertiary nitrogen on Tin(IV) molybdosilicate papers (Separation Science and Technology, U.S.A.).

3. Monitoring of organic Pollutants containing tertiary nitrogen in oil refinery effluents on Tin(IV) molybdosilicate papers (Water Research, England).

4. pH-titration and X-ray diffraction studies on the ion exchange behaviour of the synthetic crystalline silicomolybdic acid (Chemica Analityczna, Poland).

5. Synthesis, Composition and Ion exchange properties of bismuth, lead and thorium selective Tin(IV) molybdophosphate(Australian Journal of Chemistry, Australia).

6. Synthesis, dehydration studies and cation exchange behaviour of a new phase of niobium(V) phosphate (Journal of Thermal Analysis, Hungary).

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INTRODUCTION

Ion exchange is one of the most important tools for analytical chemists. It has been known since very long time. When Moses and his followers were trapped in a jungle, Moses advised his followers to cut a tree and to drop it in the bitter water. As a result the water became sweet possibly by ion exchange[1].

"They could not drink of the waters of Marah, for they were bitter.....and he cried unto Jehovah; and Jehovah showed him a tree, and he cast it into the waters, and the waters were made sweet"

(Exodus 15:23-25)

Ion exchange in soils was first noticed by Thompson[2] and Way[3]. A systematic study of ion exchange may be considered to have begun after the chance observation of Adams and Holmes[4], that crushed gramophone records show ion exchange properties.

The organic ion exchange resins could be easily synthesized with the desired capacity or degree of cross-linking and this resulted in a great advance in the theoretical aspects of ion exchange. The models which were proposed for ion exchange could be easily tested by synthesising an exchanger with the desired qualities. However, the organic resins had one great drawback i.e., they were not resistant to heat and radiations and therefore, these

materials could not be used for purification of water at high temperatures characteristic of moderator and coolant circuits in pressurized water reactors. The inorganic ion exchangers are resistant to heat and radiations and therefore they have been receiving great attention for the last forty years.

Ion exchangers are insoluble solid materials which carry exchangeable cations or anions. They have the power of acting on solutions containing ions, such as solutions of salts, and replacing some of the ions by others. In other words we may say that ion exchangers contain ions which are capable of replacement by ions from a solution containing electrolytes. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolytic solution. Carriers of exchangeable cations are called cation exchangers, and carriers of exchangeable anions, anion exchangers. Certain materials are capable of both cation and anion exchange. These are called amphoteric ion exchangers. A typical cation exchange is,

$$2\underline{\bar{X}Na} + CaCl_2\,(aq.) \rightleftharpoons \underline{Ca\bar{X}_2} + 2NaCl\,(aq.)$$

and a typical anion exchange is,

$$2\underline{\bar{X}Cl} + Na_2SO_4\,(aq.) \rightleftharpoons \underline{\bar{X}_2SO_4} + 2NaCl\,(aq.)$$

where, $\bar{X}$ represents a structural unit of the ion exchanger; solid phases are underlined; and aq. indicates that the electrolyte is an aqueous solution.

Ion exchange has many important industrial uses in addition to water softening. When hard water is passed through a suitable ion exchange resin or a zeolite, the calcium ions in water are replaced by sodium ions.

The basic types of inorganic ion exchange materials[5] are given in Table 1.

Out of the four basic types of inorganic ion exchangers presented in Table 1 the heteropoly acid salts are probably the least studied. It is, therefore, proposed to present in the following pages the salient features of heteropoly acids as inorganic ion exchangers. The heteropoly acids usually contain molybdenum or tungsten as one of the basic constituents.

Molybdenum (Mo) and tungsten (W) form numerous polymolybdate and polytungstate acids and their salts[6]. Only vanadium, niobium, tantalum and uranium show a comparable behaviour to a limited extent. The polyacids of Mo and W are of two types:

(a) The isopolyacids and their related anions which contain only Mo or W alongwith O and H.

(b) The heteropoly acids and their related anions which contain one or two atoms of another element in addition to Mo or W, O and H. All the polyanions contain octahedral MoO_6 or WO_6 groups, so that the conversion of MoO_4^{2-} or WO_4^{2-} into polyanions requires an increase in coordination number.

TABLE - 1

Basic types of inorganic ion exchange materials

A. Exchangers possessing well-defined crystal structures	(i)	Aluminosilicates
	(a)	Two-dimensional layer lattice structures, e.g., the clays and the lamellar zeolites
	(b)	Three-dimensional cage structures, e.g. the typical zeolites
	(ii)	Non-siliceous materials, e.g., heteropolyacid salts
B. Poorly crystalline and amorphous materials	(i)	Hydrous oxides of polyvalent metals
	(ii)	Acid salts of polyvalent metals and polybasic acids

Heteropolyacids are formed when molybdate and tungstate solutions containing other OXO-anions (e.g., PO_4^{3-} and AsO_4^{3-}) or metal ions are acidified. At least 35 elements are known to be capable of functioning as the hetero - atoms. The free acids and most salts of heteropoly anions are extremely soluble in water and in various organic solvents, viz. ether, alcohols and ketones. These are decomposed like the isopoly acids. They are decomposed by strong base.

$$34OH^- + [P_2Mo_{18}O_{62}]^{6-} \longrightarrow 18MoO_4^{2-} + 2HPO_4^{2-} + 16H_2O$$

$$18OH^- + [Fe_2W_{12}O_{42}]^{6-} \longrightarrow 12WO_4^{2-} + Fe_2O_3 \cdot nH_2O + 9H_2O$$

The heteropoly acids are stable without depolymerisations in strongly acid solutions; they are often themselves strong acids. In general, heteropolymolybdates and tungstates of small cations, including those of some heavy metals, are water soluble, but with larger cations insolubility is frequently found. Thus cesium, lead and barium salts are usually insoluble, and ammonium, potassium and rubidium salts are sometimes insoluble; salts of $[(\eta^5\text{-}C_5H_5)_2Fe]^+$, R_4N^+, R_4P^+ and alkaloids are invariably insoluble. Table 2 lists the principal types of heteropolymolybdates, many of which have exact or similar heteropoly tungstate analogs.

The analytical importance of heteropoly acids as ion exchangers was recognised when it was observed that if ammonium molybdophosphate (AMP) precipitate[7,8] is washed with KNO_3 solution the NH_4^+ ion is partially replaced by K^+ ion and that the washed pre-

TABLE - 2

Principal Types of Heteropoly molybdates

Ratio of hetero atoms to Mo atoms	Principal hetero-atoms occurring	Anion Formula
1:12	Series As, P, Sb, Si, Ge Sn(?), Ti, Zr	$[X^{n+}Mo_{12}O_{40}]^{(8-n)-}$
	Series Be, Co, Th, Sn(?)	$[X^{n+}Mo_{12}O_{42}]^{(12-n)-}$
1:11	P, As, Ge	$[X^{n+}Mo_{11}O_{39}]^{(12-n)-}$ (possibly dimeric)
1:10	P, As, Pt	$[X^{n+}Mo_{10}O_{X}]^{(20-60-n)-}$ (possibly dimeric)
1:9	Mn, Ni	$[X^{n+}Mo_{9}O_{32}]^{(10-n)-}$
1:6	Te, I, Co, Al, Cr, Fe, Rh	$[X^{n+}Mo_{6}O_{24}]^{(12-n)-}$
2:18	P, As	$[X_2^{n+}Mo_{18}O_{62}]^{(16-2n)-}$
2:17	P, As	$[X_2^{n+}Mo_{17}O_{X}]^{(20-102-2n)-}$
$1:6m^a$	Ni, Co, Mn, Cu, Zn, P, As	$[X^{n+}Mo_{6}O_{X}]_{m}^{m(20-36-n)-}$

a for the tungstate analog of the Cobalt (II) compound it has been found that m = 2.

cipitate may be converted to the original composition by treatment with NH_4NO_3 solution[9]. The first systematic study of ion exchange on AMP was reported by Buchwald and Thistlethwaite[10]. AMP was found to be very superior to Dowex-50 for the separation of alkali metals (Table 3).

In a more detailed study[11] several heteropoly acid salts were prepared and batch distribution coefficients were measured for the alkali metal cations, Ag^+ and Tl^+ ions at pH 2.0. The exchangers studied included ammonium molybdophosphate, molybdoarsenate, molybdosilicate, tungstophosphate, tungstoarsenate, tungstosilicate and oxine molybdophosphate. The result of the work may be summarised as follows:

(i) Under given conditions the uptake increases as the radius of the unhydrated cation increases, and in the strongly acid organic exchangers.

(ii) Tl^+ and Ag^+ ions are held more strongly than alkali metal cations of similar size, possibly indicating some degree of covalency in the bonding.

(iii) Theoretical separation factors between adjacent elements in this series are more than ten times greater than those for Dowex-50.

(iv) The distribution coefficients are almost independent of pH between 1.1 and 4.5.

(v) Multivalent cations showed negligible change in acid solution, but are strongly absorbed from neutral solutions. While

TABLE - 3

Distribution Coefficients (Kd) and Theoretical Separation Factors (α) in 0.1M NH_4NO_3 solution

$$\alpha_{A^+}^{B^+} = Kd^{B^+} / Kd^{A^+}$$

Cation	Ammonium molybdophosphate		Dowex-50	
	Kd	α	Kd	α
Na^+	0		26	1.7
K^+	3.4	68	46	1.1
Rb^+	230	260	52	1.1
Cs^+	6000		62	

yttrium and cerium appear to be absorbed as the trivalent ions, ruthenium, zirconium and niobium are apparently absorbed as complex species[12].

The parent acid of the class of heteropoly acids has the general formula[5] $H_3XY_{12}O_{40}.nH_2O$, where X may be one of the several elements including P, As and Si and Y a different element such as Mo, W and V. X-ray studies of ammonium tungstophosphate (ATP) reveal the structure (Figure 1) in which a PO_4 tetrahedron is surrounded by $12WO_6$ octahedra to form an approximately spherical anion by sharing oxygen atoms. The crystal lattice contains many such spheres, with cations and water molecules situated in the cavities between them. Both cations and water molecules are free to move within these cavities if considerations of size permit. Thus permitting exchange of cations between the crystal and the external solution NH_4^+ ions, the large monovalent cations (K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg_2^{2+}) and organic bases such as quinoline are large enough to pack stably into the structure and lower the lattice energy sufficiently to form an insoluble crystal. Salts containing other alkali metal cations are much more soluble and are unsuitable for exchange purposes.

The ion exchange behaviour of ATP is found to be the same whether it is prepared by direct precipitation of the salt from mixed molybdate and phosphate solutions or by adding NH_4NO_3 solution to the free acid. The tungstophosphate and molybdoarsenate show large variation in appearance and in values of Kd for various cations when prepared in different ways. X-ray photographs show the presence of three different structures in varying proportions

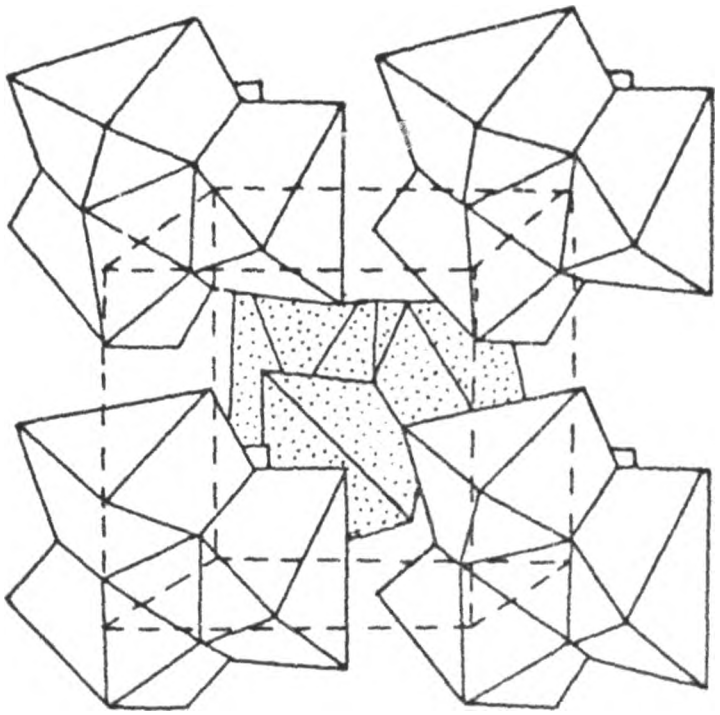

Fig. 1 Cubic unit cell of the tungstophosphate anion. Each unit cell contains two $(PW_{12}O_{40})^{3-}$ Polyhedra formed by sharing edges between WO_6 octahedra located tetrahedrally about a central P atom.

in these two salts. Only one of the structures being capable of undergoing exchange.

AMP as synthesised by Krtil and Kourim[13] showed high sorption capacity for caesium and demonstrated its adequate resistance to degradation in acidic solutions. Van R. Smit[14-16] studied the sorption of monovalent cations at trace concentrations in NH_4NO_3 media at pH=2. Their preparations of AMP gave the selectivity sequence,

$$Na^+ < K^+ < Rb^+ < Cs^+; \quad Ag^+ < Tl^+$$

This sequence is the same as the order of cation crystallographic radii. Qualitatively this is the same as the selectivity sequence of the NH_4^+ form of Dowex-50 ion exchange resin. Quantitatively the separation factors measured for the AMP were much larger than those found for Dowex-50.

Van R. Smit et al. also investigated the sorption and separation by ion exchange chromatography of macroquantities of the cations[17,18], Na^+, K^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, Cd^{2+}, VO_2^{2+}, Y^{3+} and In^{3+} on the columns of AMP with asbestos support. They have also utilised the strongly preferential retention of caesium as the basis for a large scale, AMP ion exchange process for the recovery of caesium-137 from fission product wastes[19,20].

Van R. Smit et al.[21] interpreted the barium sorption in the light of work done by Healy et al.[22] on the coprecipitation and/or ion exchange recrystallisation preparation of a variety of neutral, acid and double salts of tungstophosphoric acid with a

selection of mono-, di-, and trivalent cations.

The proposed mechanism involves a single-step cation exchange,

$$2(NH_4)_2(H_3O)[PMo_{12}O_{40}] + Ba^{2+} \rightleftharpoons Ba(NH_4)_4[PMo_{12}O_{40}]_2 + 2H_3O^+$$

which also accounts for the observed dependence of barium elution on NH_4^+ ion concentration and/or acidity.

Broadbank and coworkers[23] separated a mixture of traces of Cs^+, Sr^{2+} and Y^{3+} on a shallow bed of AMP supported on filter paper. Sr^{2+} was eluted with 0.1M HNO_3 and Y^{3+} with 1M HNO_3; Cs^+ was retained on the bed.

The demonstrated ion exchange capabilities of AMP have been applied in the development of analytical methods of separation and determination of sodium and potassium[24], and several radio nuclides in water samples[25] including cesium-137 in both fresh and sea waters[25-29]. Thin layer ion exchange chromatography methods utilizing AMP as well as other heteropoly acid salts have also been developed.

Krtil and Kourim[13] found that their analyzed AMP preparation, $(NH_4)_{2.67}H_{0.33}[PMo_{12}O_{40}]\cdot 9.5H_2O$, had a higher capacity for cesium ion and better acid stability than their AMP preparation.

Krtil regarded the acid salt, $(NH_4)_2H[PMo_{12}O_{40}]$, as a mixture of the triammonium salt and the free acid, $H_3[PMo_{12}O_{40}]$. He also prepared ion exchange chromatography columns of AMP precipitated on asbestos[30-31], for elution-separation experiments with rubidium and

cesium, in both trace ($^{86}Rb^+$, $^{134}Cs^+$, $^{137}Cs^+$) and macroamounts, and with mixtures of trace $^{137}Cs^+$, $^{90}Sr^{2+}$, and $^{90}Y^{3+}$.

In another set of experiments[32], Krtil and Krivy prepared the mixed heteropoly ammonium molybdotungstophosphate salts:

AM_4T_8P $\quad (NH_4)_{2.55}H_{0.45}[PMo_4W_8O_{40}] \cdot 6.5\ H_2O$

AM_6T_6P $\quad (NH_4)_{2.58}H_{0.42}[PMo_6W_6O_{40}] \cdot 7.6\ H_2O$

AM_8T_4P $\quad (NH_4)_{2.48}H_{0.52}[PMo_8W_4O_{40}] \cdot 5.7\ H_2O$

Broadbank and coworkers[25] prepared AMP and the corresponding potassium rubidium, cesium and mono-, di-, tri-, and tetramethylammonium salts[33]. All were found to be essentially insoluble in water and dilute HNO_3. These salts performed as efficient sorbents for traces of Cs^+, Sr^{2+}, and Y^{3+} ions, but none appeared to offer more advantages than AMP.

Several groups[34-36] have developed the technique of thin layer ion exchange chromatography on paper impregnated with AMP[34-36], ATP[34], and a selection of other heteropoly salts[33,36,39] cast on TLC plates[33]. ATP has been used for the isolation of traces of cesium by scavenger coprecipitation[40], and 20 different heteropoly- and-binary, and ternary mixed heteropoly acids have been similarly used for the cesium-francium pair[41].

The earlier work up to 1962 on the synthesis and ion exchange properties of heteropoly acids has been summarised by Amphlett[42] in

his classical book "Inorganic Ion Exchangers". The relevant literature in this field from 1962 to 1970 has been reviewed by Peterson[43] and Clearfield[44]. The work done in this area since 1970 is given in Table 4.

A study of the literature survey cited above shows that no work has yet been done on Tin(IV) molybdosilicate. Hence, the present piece of work was undertaken to devise methods for the synthesis of Tin(IV) molybdosilicate and to study its different properties as well as the separation potential. As far as crystalline silicomolybdic acid is concerned, although, it has been synthesized by many workers[89-91], however its ion exchange properties have not been studied so far. Therefore, these studies on the synthetic Tin(IV) molybdosilicate(an heteropoly acid salt) and crystalline silicomolybdic acid (an heteropoly acid) are presented in the following chapters.

TABLE - 4

Synthesis and Ion Exchange Properties of Heteropoly acid salts

S.No.	Name of the exchangers	Seperations studied	References
1.	Arsenomolybdate	-	45,46,47
2.	Cr(III)arsenophosphate	$Cd^{2+} - Ni^{2+}$, $Fe^{3+} - Cu^{2+}$, $Fe^{3+} - Ni^{2+}$, $Co^{2+} - Ni^{2+}$	48,49
3.	Tin(IV)arsenophosphate	$UO_2^{2+} - Th^{4+}$, $UO_2^{2+} - Zr^{4+}$, $Na^{+} - K^{+}$	48,49
4.	Germanomolybdate	-	45,46,47
5.	Tin(IV)molybdoarsenate	$La^{3+} - Ba^{2+}$, $Hg^{2+} - Cd^{2+}$, $Ce^{3+} - Y^{3+}$	50
6.	Ammonium molybdophosphate	^{137}Cs - Other metals	51
	-do-	^{137}Cs	52

(TABLE - 4 CONTD.)

S.No.	Name of the exchangers	Separations studied	Reference
	Ammonium molybdophosphate	Th^{4+} - UO_2^{2+}-Sp	53
	-do-	Zr^{4+} - Nb^{5+}	54
	-do-	Cs^{+}	55,56
	-do-	Cs^{+} - Radioactive waste	57
7.	Zirconium molybdophosphate	Th^{3+} - Compounds	58
	-do-	-	59
8.	Zirconium molybdovanadate	-	60
9.	Phosphoantimonic acid	Alkali metals	61
10.	Phosphomolybdate	-	45,46,47
11.	Titanium phosphosilicate	Zr^{4+}, Nb^{5+}-Cs^{+}, Pu^{4+} - other metals	62
12.	Zirconium phosphosilicate	Pu^{4+} - Zr^{4+}	63
	-do-	Nd, Ce^{4+} - Trivalent metals	64

(Table 4 contd.)

S.No.	Name of the exchangers	Separations studied	Reference
13.	Cerium phosphate sulphate	10 species of cations	65
	-do-	Trivalent rare earths	66
14.	Ammonium phosphotungstate	UO_2^{2+} - Th^{4+}	67
	-do-	Cs^+	55
15.	Silicomolybdate	-	45,46,47
16.	Ammonium silicomolybdate	Cs^+	55
17.	Pyridinium tungstoarsenate	Cs^+ - Ag^+ - Tl^+	68
18.	Organic dese-tungstoniobiosilicate	Cs^+ - Be^{2+}, Ca^{2+}, Mn^{3+}, Zr^{4+}	69
19.	Ammonium tungsto-Vanadoarsenate	Cs^+ - Rb^+	70
20.	Vanadophosphate	In^{3+} - Ga^{3+}, Mg^{2+} - Ca^{2+}, Mg^{2+} - Bi^{2+}	71

(TABLE - 4 CONTD.)

S. No.	Name of the exchangers	Separations studied	References
21.	Zirconium silicophosphate	-	72
22.	Tin(IV) molybdoarsenate	Ba^{2+} - La^{3+} Mg^{2+} - La^{3+}, Sr^{2+} - Y^{3+}, Sr^{2+} - La^{3+}	73
23.	Tin(IV) Vanadoarsenate	Some metal ions	74
24.	Zirconium arsenophosphate	Cs^{+} - Rb^{+}, Sr^{2+} - Rb^{+}, Ag^{+} - Tl^{3+}, Cd^{2+} - Ag^{+}, Cd^{2+} - Pb^{2+}, Mg^{2+} - Pb^{2+}, Sr^{2+} - Pb^{2+}, Mg^{2+} - Bi^{3+}, Ca^{2+} - Y^{3+}, Zr^{4+} - Ce^{3+}, La^{3+} - Nd^{3+}, La^{3+} - U^{6+} Tb^{3+} - Co^{3+} Th^{4+} - Ce^{3+}	75

(Table - I Contd.)

S. No.	Name of the Exchangers	Separations studied	References
		$V^{5+} - U^{6+}$; $Fe^{3+} - In^{3+} - Co^{3+}$	
25.	Pyridinium tungstoarsenate	Some metal ions	76
	-do-	Amino acids	77
26.	Titanium tungstoarsenate	$Pb^{2+} - Hg^{2+}$; $Pb^{2+} - Cu^{2+}$	78
27.	Titanium tungstophosphate	$Zn^{4+} - Pb^{2+}$; $Zn^{4+} - Cu^{2+}$; $Nd^{3+} - Sm^{3+}$	79
28.	Collidinium molybdoarsenate	Separation of Thallium	80
29.	Ammonium molybdophosphate	Aromatic amines	81
	-do-	Amino acids	82
30.	Ammonium tungstophosphate	Aromatic amines	81
	-do-	Amino acids	82

(TABLE - 4 CONTD.)

Sl. No.	Name of the Exchanger	Separations studied	Reference
31.	Cerium(IV) phosphosilicate	Ternary and binary separations of metal ions	83
32.	Tin(IV) hexacyanoferrate	-	84
33.	Tin(IV) boratomolybdate	$Th^{4+} - Zr^{4+}$, $Hg^{2+} - Cu^{2+}$, $Fe^{3+} - Cu^{2+}$, $Dy^{3+} - Zr^{4+}$, $Ce^{3+} - Mg^{3+}$, $Ce^{3+} - Mo^{3+}$, $Ce^{3+} - La^{3+}$, $Ce^{3+} - Bi^{3+}$, $Ce^{3+} - Zr^{4+}$, $Bi^{3+} - Zr^{4+}$	85
34.	Tin(IV) molybdoarsenate	$Hg^{2+} - Ca^{2+}$, $Co^{2+} - Fe^{3+}$, $Cu^{2+} - Fe^{3+}$, $Hg^{2+}-Mn^{2+}-Al^{3+}$, $Hg^{2+}-Ni^{2+}-Al^{3+}$, $Hg^{2+}-Mn^{2+}-Fe^{3+}$, $Hg^{2+}-Ni^{2+}-Fe^{3+}$	86

(TABLE - 4 CONTD.)

S.No.	Name of the Exchangers	Separations studied	Reference
		Mg^{2+}-Cu^{2+}-Al^{3+}	
35.	Tin(IV) Vanadotungstate	Al^{3+} - Cu^{3+} Al^{3+} - Fe^{3+}	87
36.	Tin(IV) arsenoantimonate	Mg^{2+} - Mn^{2+}, Ba^{2+} - Mn^{2+}, Cd^{2+} - Mn^{2+}, Ni^{2+} - Cu^{2+}	88

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CHAPTER-II

CHAPTER - II

SYNTHESIS AND ION EXCHANGE PROPERTIES OF THERMALLY STABLE AND HYDROUS Tin(IV) SELECTIVE Tin(IV) MOLYBDOSILICATE: COMPARISON WITH OTHER Tin(IV) [illegible] ION EXCHANGERS

The present status of the synthetic inorganic ion exchange materials is due to their growing applicable potentiality in the fields of medicine, energy resources recovery and in the pollution abatement.

It is an interesting feature of the heteropoly acid derivatives that their properties are different from those of the simple salts from which they may be formed. Sometimes these derivatives show superiority over their simple salts with respect to their ion exchange capacity, thermal stability and selectivity. Therefore, the investigation of these derivatives has become a current field of research.

Qureshi et al. have been investigating Tin(IV) derivatives of different heteropoly acids and have published the studies on the crystalline Tin(IV) vanadophosphate[1], Tin(IV) molybdoarsenate[2], and Tin(IV) tungstoarsenate[3,4]. S.A. Nabi and coworkers have studied Tin(IV) boratemolybdate[5]. Varshney and Khan have reported their studies on Tin(IV) arsenophosphate[6]. The ion exchange properties of Tin(IV) molybdate[7,8] and Tin(IV) silicate[9] have been described but no work has yet been done on Tin(IV) molybdosilicate. The present report summarises the synthesis and analytical utility of Tin(IV)

molybdosilicate. Its ion exchange properties have been compared with those of Tin(IV) molybdate[7,8], Tin(IV) silicate[9] and other Tin(IV) based ion exchangers.

Experimental

Chemicals and Reagents

Stannic chloride pentahydrate (J.T. Baker Chemical Co., Phillipsburg, New Jersey), Sodium molybdate dihydrate (Veb Jena Pharm, Germany), Sodium silicate (Riedel De Haen AG, Germany) and all other reagents used were of analytical grade.

Apparatus

Elico model L_1-10T pH-meter for pH-measurements, Spekol and UV-VIS/4 (ZAUM) Spectrophotometer for colorimetric determinations, muffle furnace for heat treatment, Spectromom-2000 for I.R. Spectra, thermobalance for T.G.A., Chromel-alumimal thermocouple for D.T.A. and Philips PW-1060 X-ray unit for X-ray dif-ractograms were used. Shaking was performed with a Elico temperature-controlled shaker.

Synthesis of Tin(IV) molybdosilicate

0.1M stannic chloride (2 vol) was added to a clear solution containing 0.1M sodium molybdate (1 vol) and 0.1M sodium silicate (1 vol). The pH of the mixture was nearly 1. An orange yellow coloured gelatinous precipitate of Tin(IV) molybdosilicate appeared. After aging of this precipitate for 3 hours it was refluxed in the mother liquor for 6 hours at 75°C. After refluxing the light yellow precipitate was allowed to settle for 24 hours. The precipitate was filtered, washed with demineralised water till the pH of the washing was ~ 6 and dried at 40°C in an electric oven. The light yellow dried product was immersed in demineralised water when it cracked to small granules. It was sieved to a 100-200 mesh size and immersed in 1M nitric acid to convert it into the H^+ form. The immersing acid was replaced several times with fresh 1M nitric acid till a complete conversion was achieved. The material was finally washed with demineralised water to remove excess acid and dried at 40°C. The syntheses of Tin(IV) molybdosilicate samples at various conditions are reported in Table 5 and the sample No. 5 has been selected for its detailed studies due to its highest ion exchange capacity (0.65 meq/g) and the higher yield.

Ion Exchange Capacity

Ion exchange capacities of all the samples were determined by the column operation method[10]. 0.5 g of the sample in the H^+ form was taken in the column and the H^+ ions were then eluted with 0.5M sodium chloride. The H^+ ions thus eluted, were then determined

Table - 5

Conditions of preparation and Ion Exchange Capacity of Tin(IV) molybdosilicate samples.

The reagents were 0.1M Stannic Chloride + 0.1M Sodium molybdate + 0.1M Sodium silicate in the volume ratio 2:1:1.

Sample No.	Refluxing time(hour)	pH	Appearance in the H^+ form	Ion Exchange capacity(meq/g)
1	-	1	Grey	0.45
2	-	2	Whitish grey	0.50
3	-	3	Whitish grey	0.60
4	4	1	Yellow	0.55
5	6	1	Light yellow	0.65
6	12	1	Light yellow	0.65

titrimetrically using standard sodium hydroxide solution. The ion exchange capacities of the sample with different cations were determined in the same way by taking 0.5 g of the exchanger in the H^+ form and 0.5M of each eluant. The results are shown in Table 6.

pH-Titrations

pH-titrations for LiCl-LiOH, NaCl-NaOH and KCl-KOH solvent systems were performed by the method of Topp and Pepper[11]. 0.5 g of the sample in the H^+ form was equilibrated with 50 ml of the solvent. These results are shown in Figure 2.

Chemical Stability

0.2 g of Tin(IV) molybdosilicate was kept for 24 hours in the concerned acid solutions with intermittent shaking. The undissolved material was removed. Tin(IV), Molybdenum and Silicon were determined in the filtrate. Tin(IV) was determined with 1% hematoxylin[12] and molybdenum was determined by the acetone method[13] using Spekol at 515 m μ and 420 m μ respectively. Silicon was determined by the heteropoly blue method[14] using UV-VIS spectrophotometer at 700 m μ SiO_2. These results along with the results of various other materials are given in Table 7.

Thermal Stability

The ion exchange material was heated in the muffle furnace at different temperatures for 1 hour. The effect of heat on the ion

Table - 6

Ion exchange capacity of Tin(IV) molybdosilicate for various cations

S.No.	Eluant used*	pH of the eluant	Exchanging metal ion	Ion exchange capacity (meq/g)
1.	Ammonium chloride	5.6	NH_4^+	0.45
2.	Lithium chloride	5.4	Li^+	0.40
3.	Sodium chloride	5.2	Na^+	0.66
4.	Potassium chloride	5.5	K^+	0.70
5.	Magnesium nitrate	5.7	Mg^{2+}	0.44
6.	Calcium nitrate	5.6	Ca^{2+}	0.50
7.	Strontium nitrate	5.8	Sr^{2+}	0.55
8.	Barium nitrate	5.5	Ba^{2+}	0.57

* The concentrations of all the eluants used were 0.5M.

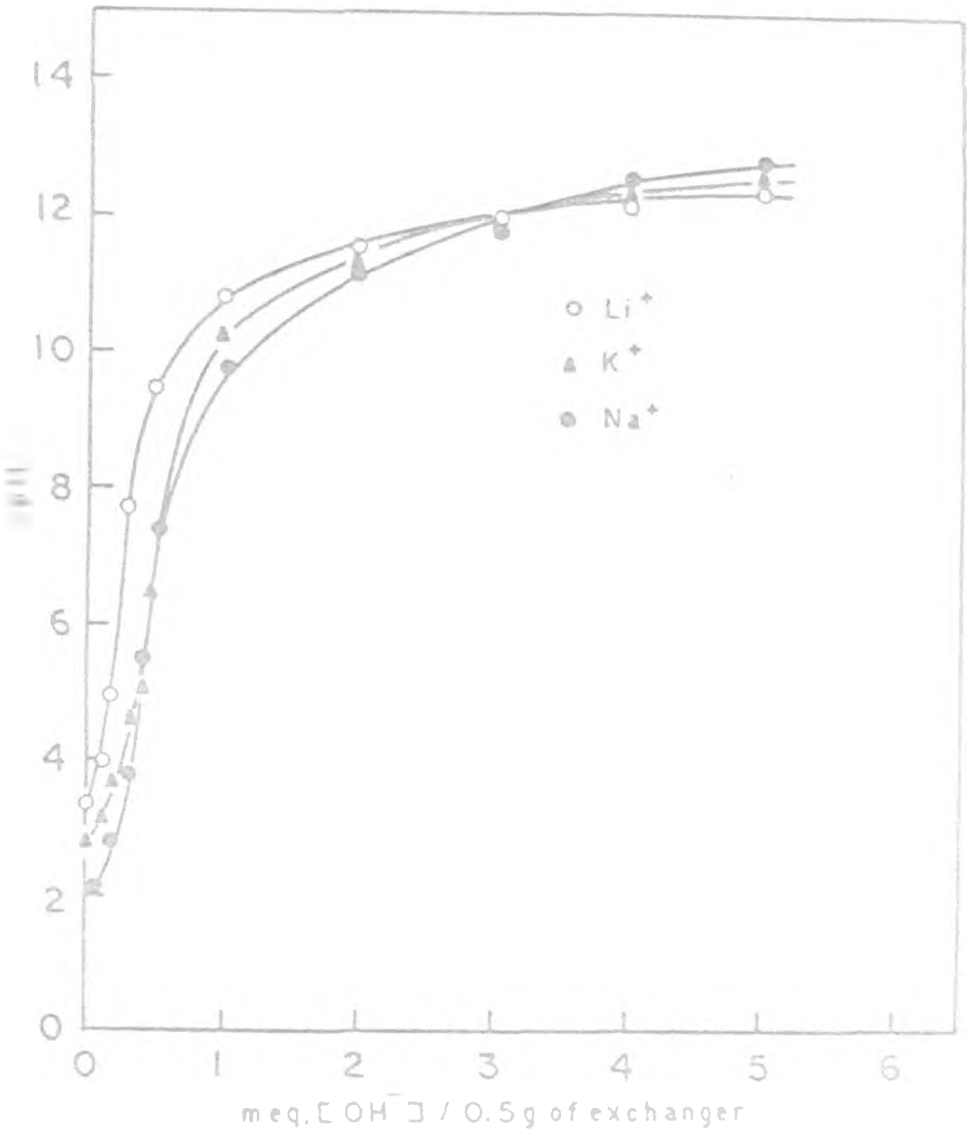

Fig. 2 pH-Titration curves of Tin(IV) molybdosilicate

TABLE - 7

Chemical Stability (mg/50 ml) of Tin(IV) derivatives of heteropoly acids

S. No.	Solvent used	Sn - Mo - Si			Sn - Mo - As			Sn - W - As			Sn - V - P			Sn - As - P	
		Sn	Mo	Si	Sn	Mo	As	Sn	W	As	Sn	V	P	Sn	As P
1.	4N HNO_3	11.00	12.00	0.80	3.60	20.00	17.00	8.00	0.60	1.00	0.00	0.00	0.00	Partially Soluble	
2.	4N HCl	15.00	140.00	0.42	Dissolved completely			145.00	11.00	47.50	0.01	0.00	16.00	Completely Soluble	
3.	4N H_2SO_4	7.50	44.00	0.30	22.50	62.50	30.00	29.00	0.40	20.00	0.00	0.30	0.10	-	

exchange capacities of Tin(IV) molybdosilicate and other Tin(IV) based ion exchangers is shown in Table 3.

I.R. Studies

I.R. spectra of the sample in the H^+ form dried at different temperatures were recorded using the Nujol technique and the results are shown in Figure 3.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of the sample in the H^+ form was performed with the heating rate of 10°C/min and the results are presented in Figure 4.

Differential Thermal analysis (DTA)

The differential thermal analysis was recorded in the atmosphere of N_2 using the chromel-alumina thermocouple and alumina as the reference material under controlled heating at the rate of 12.5°C/min. The results are shown in Figure 4.

Chemical Composition

0.3 g of the exchanger was dissolved in hydrochloric acid. Silicon was evaporated as SiF_4[15] and thus it was separated from Tin(IV) and molybdenum. Tin(IV) was determined volumetrically[16]

TABLE - 8

Effect of drying temperature on the ion exchange capacities (meq/g) of various Tin(IV) based ion exchangers

S. No.	Temperature(^{0}C)	Sn-Mo-Si	Sn-Mo	Sn-Si	Sn-V-P Samples 1, 2	Sn-As-P	Sn-Mo-As	Sn-V-As	Sn-B-Mo
1.	40	0.65	1.00	0.532	1.98, 1.70	1.75	1.20	1.10	1.12
2.	100	0.60	0.10	0.178	1.50, 1.50	1.65	0.90	-	0.33
3.	200	0.75	0.07	-	1.00, 1.10	0.90	0.60	-	0.22
4.	300	-	0.07	0.108	0.90, 0.50	-	0.51	0.51	0.17
5.	400	0.32	0.04	-	- -	0.20	0.35	-	0.15
6.	500	-	-	0.109	- -	-	-	0.31	0.08
7.	600	0.08	-	-	- -	0.10	0.20	-	0.04
8.	700	-	-	-	- -	-	0.04	-	-
9.	800	1.20	-	-	- -	0.00	-	0.04	0.00

ABBREVIATIONS

Sn-Mo-Si = Tin(IV)molybdosilicate
Sn-Si = Tin(IV)silicate
Sn-As-P = Tin(IV)arsenophosphate
Sn-V-As = Tin(IV)tungstenarsenate

Sn-Mo =Tin(IV)molybdate
Sn-V-P = Tin(IV)vanadophosphate
Sn-Mo-As= Tin(IV) molybdoarsenate
Sn-B-Mo = Tin(IV)boratomolybdate

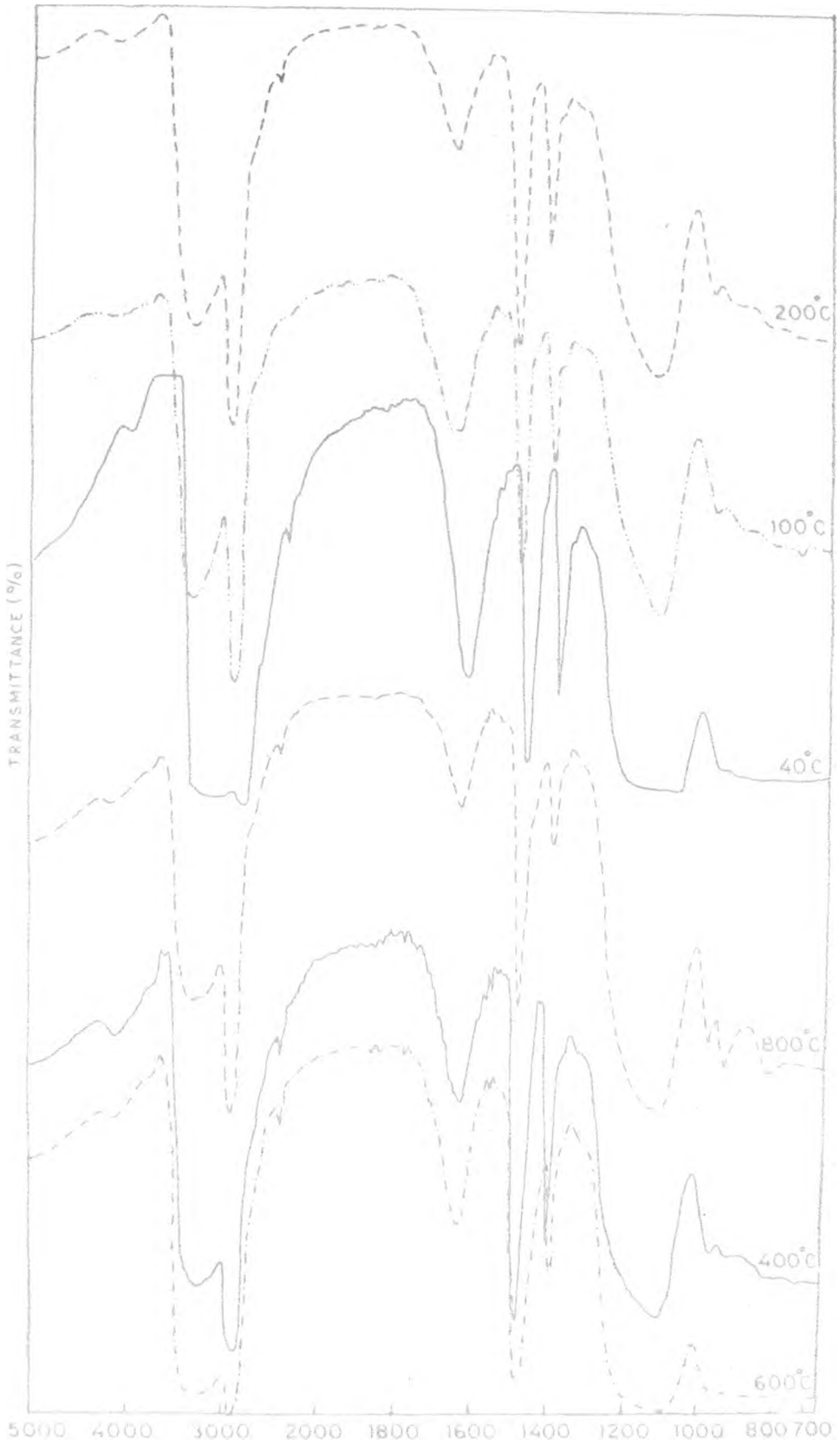

Fig. 3 I R Spectra of Tin (IV) molybdosilicate dried at different temperatures

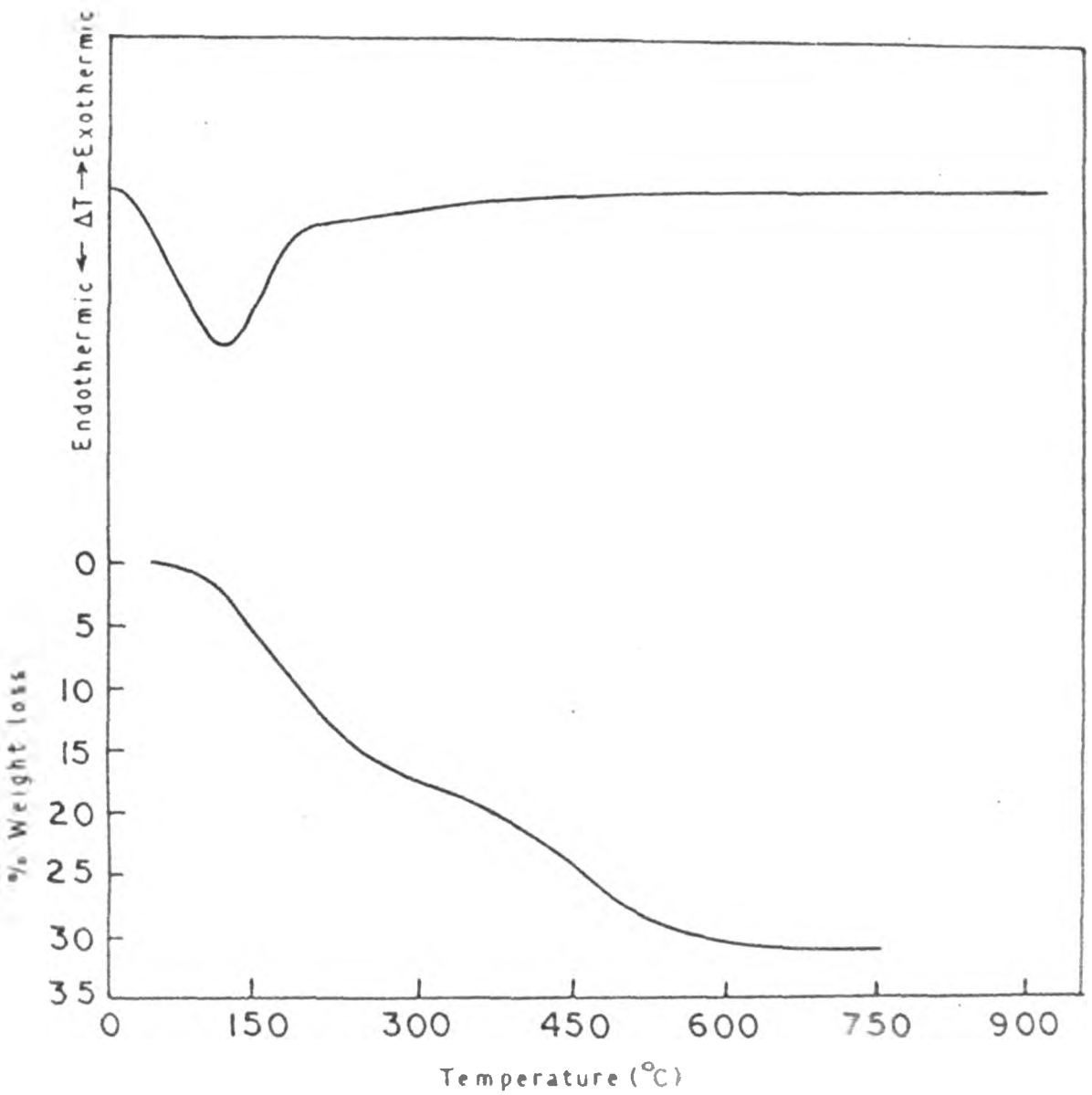

Fig 4 T.G A. and D.T A.curves of Tin (IV) molybdosilicate

and molybdenum was determined gravimetrically[17].

Distribution Coefficient Studies

The distribution coefficients (Kd) of 16 cations were determined in demineralised water, nitric acid and ammonium nitrate systems. The concentrations of all the cationic solutions were 0.001M. For this purpose 0.2 g of the exchanger was shaken with 20 ml of the solution for 24 hours. The amount of the cation in the solution was determined by titration with 0.002M ethylenediaminetetraacetic acid (EDTA) and the Kd values were calculated from the equation as follows:

$$Kd = \frac{I - F}{F} \times \frac{20}{0.2} \text{ ml/g}$$

where, I is the volume of EDTA consumed by the original solution and F is the volume of EDTA consumed after equilibrium. The results are given in Table 9.

Quantitative Separations

1.5 g of exchanger in the H^+ form was placed in a 30 x 0.39 cm (i.d.) glass column over a glass wool support. The mixture of the metal ions was recycled 5-6 times before the elution. The metal ions were then eluted by suitable eluents. The flow rate of the effluent was maintained 1 ml/min throughout the elution process. The

Table - 3

Distribution Coefficients (Kd, ml/g) of Tin(IV) molybdosilicate in different solvents.

S.No.	Metal ion	D.M.W. (pH=6.6)	0.01M HNO_3(pH=2)	0.001M HNO_3(pH=3)	0.01M NH_4NO_3(pH=2)
1.	Mg^{2+}	385	15	77.0	100
2.	Ca^{2+}	325	17	69.0	95
3.	Sr^{2+}	287	17	18.0	83
4.	Ba^{2+}	237	3	7.5	27
5.	Zn^{2+}	160	32	11.5	C.A.
6.	Cd^{2+}	80	33	33.0	167
7.	Hg^{2+}	37	2	2.5	22
8.	Bi^{2+}	300	40	17.0	283
9.	Co^{2+}	35	12	25.0	C.A.
10.	Mn^{2+}	41	0	9.0	31
11.	Cu^{2+}	C.A.	50	11.0	C.A.
12.	Pb^{2+}	375	56	400.0	C.A.
13.	Al^{3+}	C.A.	25	0.0	7

(Paper - 9 cycles)

S.No.	Metal ion	D.M.W. (pH=6.6)	0.01M HNO_3 (pH=2)	0.001M HNO_3 (pH=3)	0.01M NH_4NO_3 (pH=2)
14.	Fe^{3+}	900	25	50.0	C.A.
15.	Bi^{3+}	1350	69	42.0	243
16.	Th^{4+}	C.A.	C.A.	C.A.	C.A.

D.M.W. = Demineralized water

C.A. = Complete Adsorption

results are presented in Table 10.

RESULTS AND DISCUSSION

It is clear from Table 5 that the pH of the mixture and the refluxing time greatly affect the ion exchange capacity as well as the appearance of the material. It can be inferred that an increase in the pH of the mixture increases the ion exchange capacity of the material. When Sample No.1 (at pH = 1) is refluxed for 4 hours an increase in the ion exchange capacity has been observed. The ion exchange capacity further increases when the mixture is refluxed for 6 hours under identical conditions. However, further increase in the refluxing time does not affect the ion exchange capacity of the material. Sample No.5 has been chosen for detailed studies because of its high apparent stability, considerable ion exchange capacity (0.65 meq/g) and the higher yield.

Table 6 shows the ion exchange capacity for alkali and alkaline earth metal ions. The trends for the variation in the ion exchange capacity are different in Tin(IV) molybdate[7,8] and Tin(IV) molybdosilicate. The ion exchange capacity data show that the exchange of ions takes place in the hydrated and the unhydrated forms of counter ions.

pH-titration curves (Figure 2) of Tin(IV) molybdosilicate show some interesting features. The uptake of the Na^+ ion is higher than that of the K^+ ion and the Li^+ ion below pH 4. The uptake of

TABLE - 10

Separations achieved on Tin(IV) molybdosilicate column

S.No.	Mixture loaded (1.5+2.5)ml	Cation eluted	Eluant	Amount loaded (µg)	Amount recovered (µg)	Error (%)
1.	$Hg^{2+}+Zn^{2+}$	Hg^{2+}	A	301.0	284.0	-5.65
		Zn^{2+}	B	163.0	157.0	-3.68
2.	$Hg^{2+}+Cd^{2+}$	Hg^{2+}	A	301.0	286.0	-4.98
		Cd^{2+}	B	281.0	293.0	+4.27
3.	$Mn^{2+}+Al^{3+}$	Mn^{2+}	A	82.4	85.0	+3.16
		Al^{3+}	B	67.5	65.0	-3.70
4.	$Mn^{2+}+Ni^{2+}$	Mn^{2+}	A	82.4	87.0	+5.58
		Ni^{2+}	B	146.8	134.3	-8.51
5.	$Mn^{2+}+Zn^{2+}$	Mn^{2+}	A	82.4	76.0	-7.77
		Zn^{2+}	B	163.0	155.0	-4.91
6.	$Fe^{3+}+Al^{3+}$	Fe^{3+}	A	83.8	79.5	-5.13
		Al^{3+}	B	67.5	64.0	-5.18

(TABLE - 10) CONTD.

S.No.	Mixture loaded (1.5+2.5)ml	Cation eluted	Eluant	Amount loaded (μg)	Amount recovered (μg)	Error (%)
7.	$Fe^{3+}+Zn^{2+}$	Fe^{3+}	A	83.8	76.5	-8.71
		Zn^{2+}	B	163.0	157.0	-3.68
8.	$Fe^{3+}+Cd^{2+}$	Fe^{3+}	A	83.8	80.0	-4.53
		Cd^{2+}	B	281.0	290.0	+3.20

* = All the cation solutions used were 0.001M

A = Demineralised water

B = 0.001N HNO_3

the Na^+ ion and the K^+ ion is almost equal but greater than the Li^+ ion in the pH-range 4-8. This conclusion is also confirmed from the ion exchange capacity data (Table 6). However, above pH 8 the uptake order again becomes $Na^+ > K^+ > Li^+$. The pH-titration curves reveal the monofunctional behaviour of Tin(IV) molybdosilicate.

The chemical stability of Tin(IV) molybdosilicate has been determined in different solvents as shown in Table 7. Tin(IV) molybdosilicate was found to be quite stable as compared to Tin(IV) vanadophosphate[1], Tin(IV) molybdoarsenate[2] and Tin(IV) tungstoarsenate[3].

A comparison of the ion exchange capacities of different Tin(IV) based ion exchangers at different drying temperatures is shown in Table 8. The ion exchange capacities of all the exchangers decrease when the drying temperature is increased. However, in the case of Tin(IV) molybdosilicate it is found that it shows a considerable increase in its ion exchange capacity from 0.65 meq/g at 40°C to 1.20 meq/g at 800°C.

The I.R. spectra (Figure 3) of Tin(IV) molybdosilicate in the H^+ form have been recorded at various temperatures. The I.R. spectrum of the sample at 40°C shows three strong peaks in the regions 3400-2850 cm^{-1}, 1730-1580 cm^{-1} and 1200-1000 cm^{-1}. The first peak in the region 3400-2850 cm^{-1} is due to the Nujol as well as the hydroxyl groups. The second peak in the region 1730-1580 cm^{-1} with a maximum at 1620 cm^{-1} may be due to the structural water molecules. The third peak in the region 1200-1000 cm^{-1} may be attributed to the molybdenum-hydroxyl bond. However, no change in the I.R. spectra has been observed upto 800°C.

The T.G.A. and the D.T.A. curves of Tin(IV) molybdosilicate are shown in Figure 4. The weight loss is observed from 50°C which continues up to 800°C. This may be assigned due to the loss of external water molecules. An endothermic peak is observed in this region in the D.T.A. curve which confirms the weight loss. However, after 600°C the weight becomes constant. It can be inferred that the material is not decomposed and no structural water molecules are lost in this range of temperature since Tin(IV) molybdosilicate retains the exchangeable hydrogen ions up to 800°C (Table 8). This is also confirmed from the I.R. spectra (Figure 3) which show no change in the peaks when the material is heated upto 800°C.

The chemical composition of the sample shows that Tin(IV), molybdenum and silicon are in the mole ratio of 4:1:2. However, the X-ray diffraction patterns of all the samples synthesized under different conditions show an amorphous nature.

The distribution coefficients of different metal ions in demineralized water, various concentrations of nitric acid and 0.01M ammonium nitrate systems are shown in Table 9. It is clear from the table that the adsorption of the metal ions decreases with an increase in nitric acid concentration as usual. However, this effect is more pronounced in the case of Mg^{2+}, Mn^{2+} and Al^{3+}. The Kd values almost drop to zero in 0.1M nitric acid. It is interesting to note that the adsorption of Co^{2+} is low in demineralized water but it is less affected when the concentration of nitric acid is increased. It is also important to compare the adsorption of metal ions in demineralized water and 0.01M ammonium nitrate systems. The comparison reveals that in most of the cases adsorption

is either less affected or not affected at all (e.g., Zn^{2+}, Co^{2+}, Pb^{2+} and Fe^{3+}) in both the systems except in the case of Al^{3+} where Kd value is almost negligible in 0.01M ammonium nitrate. However, the adsorption of Th^{4+} is very high and is not affected even by 0.01M nitric acid.

This differential ability for the uptake of metal ions has been utilised for some important quantitative separations as shown in Table 10. The recoveries of these ions are in the range of experimental error. The adsorption of Th^{4+} is very high and it can not be eluted even by 2M nitric acid. However, Th^{4+} can be determined by destroying the exchanger. This unusual adsorption of Th^{4+} on Tin(IV) molybdosilicate can be utilised for the recovery of Th^{4+} from thorium-containing ores.

Owing to the small Kd value of Hg^{2+} Tin(IV) molybdosilicate can be used for the selective filtration of this ion prior to its determination in the polluted water and other media. As Hg^{2+} is an important pollutant it is possible that Tin(IV) molybdosilicate may find applications in the separation of this ion from other pollutants.

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CHAPTER-III

CHAPTER - III

SEPARATION OF CERTAIN ORGANIC POLLUTANTS CONTAINING TERTIARY NITROGEN ON Sn(IV) MOLYBDOSILICATE PAPERS

Inorganic ion exchangers have long been used for the separation of cations and anions. A survey of literature shows that they have least been used for the separation of organic pollutants. Therefore, in continuation to our previous work[1-4], the papers impregnated with tin(IV) molybdosilicate have been employed for the chromatographic studies of organic pollutants containing tertiary nitrogen which are of immense physiological importance[5-7]. Use of impregnated papers proved to be more sensitive and selective and gave better resolution. The present chapter briefs the chromatographic behaviour of organic pollutants, their separations and certain important isomeric differentiation.

EXPERIMENTAL

Chromatography

Development was performed in 20 x 5 cm glass jars, using the ascending method on 14 x 3 cm. Whatman No.1 paper strips. UV-lamp was used for irradiating the spot.

Reagents

Aqueous solutions (0.1M) of stannic chloride, sodium molybdate, sodium silicate and aqueous or ethanolic solutions (1M) of the test substances were prepared. Saturated solution of copper iodide in acetonitrile and aqueous saturated solutions of sodium carbonate and phosphomolybdic acid were also prepared. All chemicals and reagents were of Analar grade obtained from BDH (England), SIGMA (U.S.A.) and E.Merck (Darmstadt) except: bavistin [2-(methoxycarbonyl) benzenidazole 50% w/w; adjuvants + add 100% w/w] and calixin (N-tridecyl-2,6-dimethylmorpholine + 80% w/w; adjuvants 20% w/w), [illegible], Aktiengesechaft, west Germany. Whatman No.1 filter paper.

Impregnation of Impregnated Papers

Paper strips were first passed through stannic chloride solution for 3-5 seconds; the excess of stannic chloride solution was removed by placing the paper strips on an ordinary filter paper sheet. The strips were then dipped in sodium molybdate and sodium silicate solutions, respectively for the same period. The strips were dried at room temperature, washed three times with demineralised water in order to remove the excess reagent and were finally allowed to dry at room temperature.

[illegible]

The paper strips were spotted for the pollutants, hung in the glass jars and developed in demineralised water and in various types

of organic and inorganic solvents. The pollutants were detected as yellow spots by dipping in the solution of phosphomolybdic acid or by dipping in the solutions of copper iodide (in acetonitrile) and sodium carbonate (aqueous) followed by irradiation with UV-light.

RESULTS

The chromatographic behaviour of the following 12 pesticides (P) and toxicants (T)(organic pollutants) has been studied:

1. (P) Amitrole (3-amino-1, 2,4-triazole),
2. (P) Azobenzene (Diphenyldiazene),
3. (P) Bavistin (2-methoxy-carbonyl benzimidazole),
4. (P) Calixin (N-tridecyl-2,6-dimethyl morpholine),
5. (T) 2,4-Lutidine (2,4-dimethyl pyridine),
6. (T) 2,6-Lutidine (2,6-dimethyl pyridine),
7. (T) N-ethylmorpholine,
8. (T) β-Picoline (3-methyl pyridine),
9. (T) γ-picoline (4-methyl pyridine),
10. (T) Pyridine,
11. (T) Quinoline, and
12. (T) Trimethylamine.

The following 21 developers (solvent systems) used were:

1. Demineralised water (D.M.W.),
2. 2%, 1%, 0.1% HCl,
3. 2%, 1%, 0.1% HNO_3,
4. 2%, 1%, 0.1% NaOH,
5. 2%, 1%, 0.1% KOH,
6. 2%, 1%, 0.1% NaCl,
7. 2% $NaNO_2$,
8. 2% $NaNO_3$,
9. 2% NaH_2PO_4,
10. 2% $KHSO_4$,
11. 2% Na_2CO_3,
12. 2% $Pb(NO_3)_2$,
13. 1% CH_3COONH_4,
14. CH_3COOH + CH_3COONH_4 (1:1%),
15. CH_3COOH + NH_4OH (1:1%),
16. NH_4Cl + NH_4OH (1:1%),
17. Benzene,
18. Carbontetrachloride,
19. Chlorobenzene,
20. Chloroform, and
21. Butylalcohol.

The result obtained is illustrated in Figure 5 by plotting R_f values against the solvents used. On the basis of the R_f values, several binary and ternary separations have been achieved which are summarised in Tables 11 and 12 respectively.

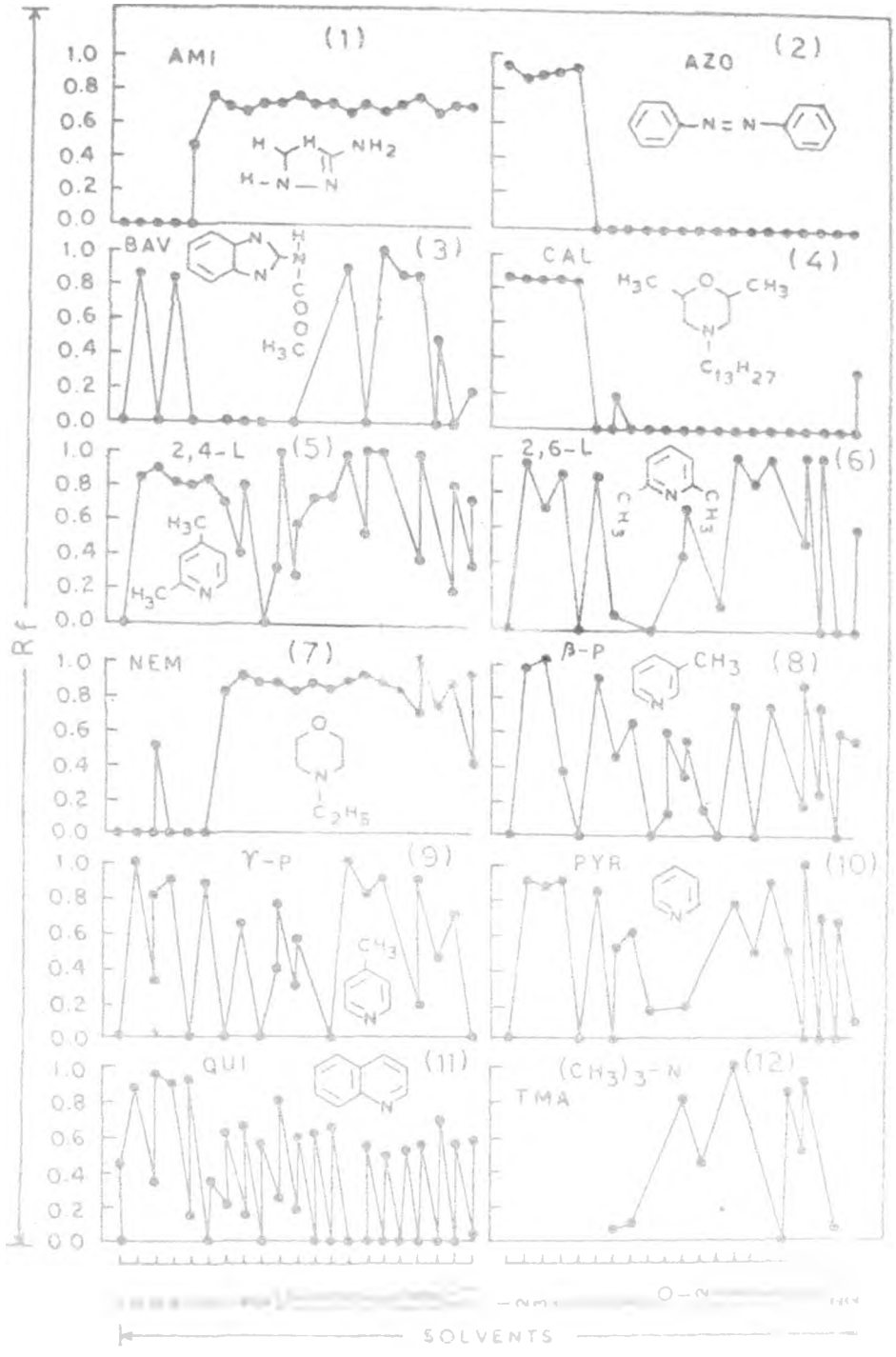

Fig. 5 R_f Values of certain organic pollutants in different solvents.
Abbreviations are defined in Table 11
Order of the solvents used is the same as in Table 11.

TABLE - 11

Binary Separations Achieved on Tin(IV) molybdosilicate papers

S.No.	Solvents	Separations		
1.	C_6H_6	AZO	——	[illegible]
		1.00		(0.00 to 7.20)
		AZO	——	β-p
		1.00		0.40
		AZO	——	γ-p
		1.00		0.15
		AZO	——	AMI
		1.00		0.00
		AZO	——	BEH
		1.00		0.00
		AZO	——	TMA
		1.00		0.00
		AZO	——	2,4-L
		1.00		0.40
		AZO	——	2,6-L
		1.00		0.00
		AZO	——	[illegible]

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
		1.00		0.00
		ABD	——	BAV
		1.00		0.00
		CAL	——	β-P
		1.00		0.40
		CAL	——	γ-P
		1.00		0.15
		CAL	——	AMI
		1.00		0.00
		CAL	——	MEM
		1.00		0.30
		CAL	——	ZNA
		1.00		0.00
		CAL	——	2,4-L
		1.00		0.40
		CAL	——	2,6-L
		1.00		0.00
		CAL	——	PYR
		1.00		0.15

(TABLE II CONTD.)

S.No.	Solvents	Separations		
2.	CCl_4	ANI	——	QUI
		0.00		1.00
		ANI	——	2,4-L
		0.00		1.00
		ANI	——	2,6-L
		0.00		0.22
		ANI	——	β-P
		0.00		0.20
		ANI	——	CAL
		0.00		1.00
		ANI	——	BAV
		0.00		1.00
		ANI	——	AZO
		0.00		1.00
		NEM	——	γ-P
		0.00		0.85
		MEM	——	AZO
		0.00		1.00
		NEM	——	2,4-L
		0.00		0.33

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
3.	C_6H_5Cl	BAV	——	PYR
		0.00		0.20
		BAV	——	CAL
		0.00		1.00
		BAV	——	AZO
		0.00		1.00
		ANT	——	PYR
		0.00		0.20
		ANT	——	AZO
		0.00		1.00
		ANT	——	QUI
		0.00		(1.90 to 3.00)
		ANT	——	β-C
		0.00		0.35
		ANT	——	γ-C
		0.00		0.25
		ANT	——	2,6-L
		0.00		0.10

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
		AMI	——	2,4-L
		0.00		0.10
4.	$CHCl_3$	AMI	——	AAO
		0.00		1.00
		AMI	——	QUI
		0.00		(4.00 to 8.50)
		AMI	——	2,6-L
		0.00		0.20
		NBM	——	AZO
		0.00		1.00
		NBM	——	QUI
		0.00		0.90
		NBM	——	γ-P
		0.00		0.30
5.	C_4H_9OH	BAV	——	QUI
		0.00		(4.30 to 8.50)
		BAV	——	AZO
		0.00		1.00

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
		β-P	———	ANI
		0.15		0.70
		β-P	———	AZO
		0.00		1.00
		γ-P	———	NEH
		0.00		0.55
		γ-P	———	QUI
		0.00		(4.50 to 8.20)
		γ-P	———	AZO
		0.20		1.00
		FXR	———	AZO
		0.00		1.00
		FXR	———	QUI
		0.00		(3.80 to 8.60)
		2,4-L	———	2,6-L
		0.75		0.00

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
6.	DMW	AZO	——	2,4-L
		0.00		0.30
		AZO	——	2,6-L
		0.00		0.40
		AZO	——	β-P
		0.00		0.35
		AZO	——	γ-P
		0.00		0.30
		AZO	——	PYR
		0.00		0.50
		AZO	——	ANI
		0.00		0.70
		QUI	——	ANI
		0.20		0.80
		QUI	——	γ-P
		0.15		0.45 → 80%
7.	2% HCl	ANI	——	GAL
		0.55		0.00

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
8.	2% HNO_3	GAL	——	MEM
		0.00		0.30 → 90%
		GAL	——	AMI
		0.00		0.65
		BAV	——	MEM
		0.00		0.50
9.	2% NaH_2PO_4	AMI	——	2,6-L
		0.20		0.35 → 80%
		AMI	——	BAV
		0.80		0.00
		AMI	——	AZO
		0.65		0.00
		AMI	——	GAL
		0.75		0.00
		PYR	——	BAV
		0.22		0.00
		PYR	——	AZO
		0.45		0.00

(Table II Contd.)

S.No.	Solvents	Separations		
		HEM	—	AZO
		0.38		0.00
10.	2% $KMnO_4$	AZO	—	QUI
		0.00		0.15
		AZO	—	ANI
		0.00		0.57
		AZO	—	β-Np
		0.00		0.45
		AZO	—	γ-Np
		0.00		0.45
		AZO	—	THA
		0.00		0.65
		AZO	—	2,4-L
		0.00		0.60
		AZO	—	2,6-L
		0.00		0.40
		AZO	—	BAV
		0.00		0.60

(Table 11 cont.)

Table	Solvents	Separations		
		AZO	——	PYR
		0.00		0.35
		GAL	——	ANT
		0.00		0.63
		GAL	——	NEM
		0.00		0.60
		GAL	——	PYR
		0.00		0.55
		GAL	——	β-NAP
		0.00		0.40
		GAL	——	γ-NAP
		0.00		0.40
		GAL	——	2,4-DNT
		0.00		0.45 → 80%
		QUI	——	NEM
		0.50		0.81
11.	2% $Pb(NO_3)_2$	NEM	——	GAL
		0.15		0.00
		NEM	——	BAP
		0.20		0.00

(TABLE II CONTD.)

S.No.	Solvents	Separations		
		HSM	———	ANI
		0.20		0.00
12.	2% NaOH	ANI	———	HSM
		0.00 to 2.30		0.25
		AZO	———	TMA
		0.00		0.25
13.	2% KOH	AZO	———	HSM
		0.00		2.20 to 6.20
		AZO	———	2,4-L
		0.00		0.26
		AZO	———	2,6-L
		0.00		2.00 to 5.60
		ANI	———	AMI
		0.00		0.10
		AZO	———	PYR
		0.00		0.25
		CAL	———	AMI
		0.15		0.55

(Table 11 Contd.)

Table.	Solvents	Separations		
		β-ala	———	HBA
		0.60		0.15
14.	2% Na_2CO_3	AZO	———	PYR
		0.00		0.70
		CAL	———	AMI
		0.35		0.12
		CAL	———	2,4-A.
		0.25		0.47
		CAL	———	PYR
		0.35		0.55
15.	2% HCl	AZO	———	β-ala
		0.00		0.25
		AZO	———	γ-ab
		0.00		0.20
		AZO	———	PYR
		0.00		0.20
		AZO	———	HBA
		0.00		0.30

(Table 11 cont'd.)

Solv.	Solvents	Separations		
		AZO	———	2,4-L
		0.00		0.30
		AZO	———	2,6-L
		0.00		0.22
		AZO	———	QUI
		0.00		2.30 to 6.10
		AZO	———	ANI
		0.00		0.53
		ANI	———	BAY
		0.66		0.00 to 3.60
		ANI	———	QUI
		0.65		2.70 to 5.30
		ANI	———	CAL
		0.60		0.00
		ANI	———	HBA
		0.65		0.00
		CAL	———	2,4-L
		0.00		0.85
		CAL	———	PIA
		0.00		1.00

(TABLE 11 CONTD.)

S.No.	Solvents	Separations		
16.	25% H_2SO_4	CAL	——	AAI
		0.00		0.50
		CAL	——	TMA
		0.00		0.05
		CAL	——	MEA
		0.00		0.32
		AAI	——	ASU
		0.70		0.00
		AAI	——	BAV
		0.55		0.00
17.	25% H_2SO_4	AZO	——	AAI
		0.00		0.67
		AZO	——	β-N
		0.00		0.55
		AZO	——	γ-N
		0.00		0.60
		AZO	——	2,4-N
		0.00		0.60

(TABLE II CONTD.)

S.No.	Solvents	Separations		
		GAL	——	β-2
		0.00		0.60
		GAL	——	AGL
		0.00		0.64
		GAL	——	PYR
		0.00		0.75
		GUI	——	AMI
		0.70 to 4.20		0.64
18.	$NH_4OH + NH_4Cl$ (1:1%)	AMI	——	AZO
		0.60		0.00
		AMI	——	GAL
		0.48		0.00
19.	CH_3COONH_4 (1%)	AZO	——	AMI
		0.00		0.65
		AZO	——	β-2
		0.00		0.85
		AZO	——	γ-2
		0.00		0.73

(TABLE 11 CONTD.)

No.	Solvents	Separations		
		CAL	—	β-C
		0.00		0.78
20.	$CH_3COOH + NH_4OH$ (1:1%)	AM	—	AM
		0.61		0.00
		AM	—	QUI
		0.60		2.00 to 4.20
		QUI	—	NIC
		1.60 to 6.00		1.00
		QUI	—	CAL
		0.40		0.00 → 90%
		QUI	—	γ-C
		0.35		0.53
21.	$CH_3COOH + CH_3COONH_4$ (1:1%)	β-C	—	AZO
		0.65		0.00
		β-C	—	AM
		0.50		0.75

(TABLE II CONTD.)

S.No.	Solvents	Separations	
		β-P	OAL
		0.55	0.00 to 2.60
		γ-P	AZO
		0.68	0.00
		OAL	AZO
		0.00	0.60

ABBREVIATIONS

AMI	= Amitrole	MEM	= N-ethylmorpholine
AZO	= Azobenzene	β-P	= β-Picoline
BAV	= Bavictin	γ-P	= γ-Picoline
OAL	= Calixin	PYR	= Pyridine
2,4-L	= 2,4-Lutidine	QUI	= Quinoline
2,6-L	= 2,6-Lutidine	TMA	= Trimethylamine

Table - 12

Ternary Separations Achieved on Tin(IV) Molybdosilicate Papers

Sl.No.	Solvents					
1.	C_6H_6	AZO	—	GAL	—	β-I
		1.00		0.00		0.17
		AZO	—	GAL	—	γ-I
		1.00		0.00		0.20
		AZO	—	GAL	—	HBA
		1.00		0.00		0.21
		AZO	—	GAL	—	BAV
		1.00		0.00		0.10
		AZO	—	GAL	—	2,6-L
		1.00		0.00		0.15
		AZO	—	GAL	—	PYR
		1.00		0.00		0.16
2.	DMF	AZO	—	AMI	—	2,4-L
		0.00		0.65		0.30
		AZO	—	AMI	—	γ-I
		0.00		0.75		0.34

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(Table 12 contd.)

S.No.	Solvents	Separations				
3.	2% HNO_3	GAL	—	AMI	—	TMA
		0.00		0.55		0.10
		GAL	—	β-P	—	TMA
		0.00		0.41		0.10
4.	2% $KHSO_4$	GAL	—	2,4-L	—	NEM
		0.00		0.65		0.42
		GAL	—	γ-P	—	NEM
		0.00		4.5oto 6.5o		0.35
5.	2% KOH	GAL	—	AMI	—	NEM
		0.20		0.60		0.70
6.	2% $NaNO_3$	GAL	—	AMI	—	NEM
		0.00		0.55		0.70
		AZO	—	AMI	—	NEM
		0.00		0.65		0.75
		BAV	—	AMI	—	NEM
		0.00		0.70		0.80
7.	1% CH_3COONH_4	GAL	—	AMI	—	NEM
		0.00		0.60		0.70

(Table 12 Cont'd.)

S.No.	Solvents	Separations				
8.	$CH_3COOH + NH_4OH$ (1:1%)	2,6-L	—	AM	—	DL
		0.30		0.60		0.00
9.	$CH_3CH(NH_2)CH_2COOH$ (1:1%)	DL	—	AM	—	β-A
		0.00		0.60		0.45

Abbreviations are given in Table 11

Discussion

Application of paper chromatography for the separation of organic pollutants containing tertiary nitrogen is well documented[8,9]. Since the publication of inorganic ion exchangers by Amphlett, interests have been in synthesizing new inorganic ion exchangers and exploring the possibility of using them in inorganic paper chromatography[10-12]. These impregnated papers are more selective than unimpregnated papers and the separations on these papers are fast, predictable and reproducible. The separation potential of the papers impregnated with synthetic inorganic ion exchangers has not been fully explored and so far as we are aware that Tin(IV) molybdosilicate papers have not been used for the separation of organic pollutants containing tertiary nitrogen. Therefore, these papers were employed for their separations. It was found that several separations which were difficult on unimpregnated papers were achieved by using the impregnated papers. Wagner and Lehmann[13] have used saturated solution of copper iodide in acetonitrile, saturated solution of sodium carbonate in water followed by UV-radiation for the detection of heterocyclic nitrogen compounds by fluorescence. Use of the saturated solution of phosphomolybdic acid in water, in most of the cases proved to be complementary detector. Therefore, these two detectors were used in our entire course of study. From figure 5 it is clear that maximum number of separations can be achieved in non-polar solvents and minimum number in acidic solvents. For example, 18 binary separations and 6 ternary separations were achieved in benzene solvent system while only 3 binary and 2 ternary separa-

tions were achieved in acidic solvent systems. Figure 5 also indicates that mobility of Amitrole and N-ethylmorpholine is very low in organic solvents in contrast to Azobenzene and Calixin. The peculiar chromatographic behaviour of quinoline may be attributed to its fused ring system. Pyridine and its derivatives show similar behaviour which is quite logical. The results give relevant information about several binary and ternary separations.

The next and perhaps the most important aspect of this work was to attempt at isomeric differentiation and ternary separations which could not be done on unimpregnated papers. Separations of 2, 4-Lutidine from 2,6-Lutidine was successfully achieved on the impregnated papers in butylalcohol so, the method can be used for the differentiation of these isomers on the basis of their R_f values and characteristic fluorescence. Furthermore, none of the ternary separations could be achieved on the unimpregnated papers. The strong influence of various cations and anions on the R_f values can be rectified by solvent extraction using chloroform. Therefore, the method developed can be successfully used for the monitoring of these biocides in samples of air, water and soil. This method was found to be successful for the analysis of effluents of oil refinery[14].

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CHAPTER-IV

CHAPTER - IV

MONITORING OF ORGANIC POLLUTANTS CONTAINING TERTIARY NITROGEN BY OIL REFINERY EFFLUENTS ON Zn(IV) MOLYBDOPHOSPHATE PAPERS

Organics containing tertiary nitrogen are ubiquitous air, water and soil pollutants[1-5]. They are the worst offenders of the environmental peace and the ecological balance as they are depressants to the central nervous system (CNS) and are skin irritants. They cause disturbances to the respiratory tract and gastro-intestinal systems (GIS). They also damage kidneys and liver and are suspected carcinogens. They diminish growth of N_2-fixers and their viability as well as functional ability to fix atmospheric nitrogen. They are added to the environment as a result of degradation of proteinaceous materials, industrial wastes and as chemicals used in our agricultural practices[3,6]. A number of methods have been employed for the detection, determination and separation of these pollutants[7-18]. In a developing country like India there is an immense need of simple and inexpensive methods for pollution monitoring and control. Therefore, in continuation of our previous work[19-21] a new simple and inexpensive procedure has now been presented in this chapter for the monitoring of these biocides in the effluents of oil refinery prior to discharge into the main water stream. This technique was employed on the papers impregnated with Zn(IV) molybdo-

silicate.

EXPERIMENTAL

Samples of water were collected from the main effluents collector of Oil Refinery, Barauni Division, Begusarai, Bihar (India).

Reagents

Aqueous solutions (0.1M) of stannic chloride, sodium molybdate and sodium silicate. Saturated solution of copper iodide in acetonitrile and aqueous saturated solution of sodium carbonate. All chemicals and reagents were of ANALAR grade obtained mainly from BDH (England) and SIGMA (U.S.A.). Whatman No.1 filter paper.

Apparatus

Ordinary 20 x 5 cm glass jars were used to develop the paper 14 x 3 cm strips. Separating funnel was used for the extraction and UV-lamp for irradiation of the spot.

Preparation of Impregnated Papers

Paper strips were first passed through stannic chloride solution for 2-3 seconds; the excess of stannic chloride solution was removed by keeping the paper strips on an ordinary filter paper sheet. The strips were then dipped in sodium molybdate and sodium

silicate solutions, respectively for the same period. The strips were dried at room temperature, washed three times with demineralised water in order to remove the excess reagent and finally allowed to dry at room temperature.

Procedure

A sample of 80 ml after preliminary filtration was placed in a separating funnel. 1 ml of aqueous 1M NaOH and 20 ml of chloroform were added to it. After thorough shaking, chloroform layer was collected in a sample bottle. Then the papers (impregnated with tin(IV) molybdosilicate) were spotted for the pollutants, hung in the glass jars and developed in demineralised water (DMW) and in various types of organic and inorganic solvents. The pollutants were detected as bright fluorescent spots by dipping the strips in the solutions of copper iodide (dissolved in acetonitrile) and aqueous sodium carbonate, respectively, followed by irradiation with UV-light.

Results

The chromatographic behaviour of the sample has been studied in the following 21 solvents:

1. Benzene,
2. Carbon tetrachloride,

3. Chloroform,
4. Chlorobenzene,
5. Butyl alcohol,
6. Demineralised water (DMW),
7. 2%, 1%, 0.1% HCl,
8. 2%, 1%, 0.1% HNO_3
9. 2%, 1%, 0.1% NaOH,
10. 2%, 1%, 0.1% KOH,
11. 2%, 1%, 0.1% NaCl,
12. 2% NaH_2PO_4,
13. 2% $Pb(NO_3)_2$,
14. 2% Na_2CO_3,
15. 2% $KHSO_4$,
16. 2% $NaNO_2$
17. 2% $NaNO_3$
18. 1% CH_3COONH_4
19. CH_3COOH + CH_3COONH_4 (1:1%),
20. CH_3COOH + NH_4OH (1:1%), and
21. NH_4OH + NH_4Cl (1:1%)

The result obtained is illustrated in Figure 6 by plotting R_f values against the solvent systems used.

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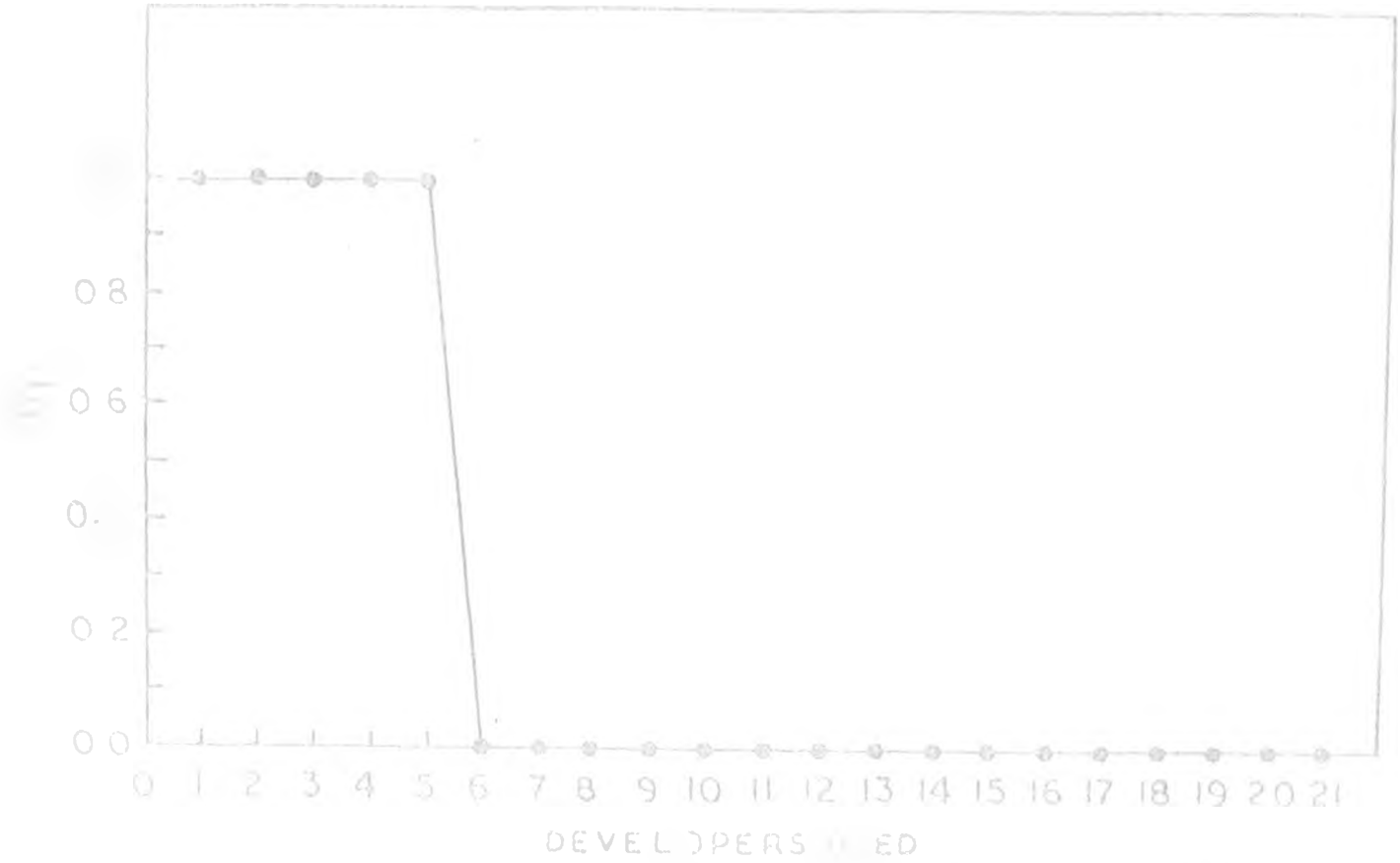
Simple paper techniques for the detection and separation of organics containing tertiary nitrogen are well documented[22-24]. Solvent extraction with chlorosolvents in basic medium has been



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used for the extraction of the organics[23]. Wagner and Lehmann[9] have used saturated solution of copper iodide in acetonitrile, aqueous saturated solution of sodium carbonate followed by UV-irradiation for the detection of heterocyclic nitrogen compounds by fluorescence. As the techniques developed earlier have not been used for actual samples, therefore, prior to the detection, the pollutants were extracted by chloroform. Moreover, method developed by Qureshi et al.[19] was found to be good enough for the field detection but not for chromatographic studies. Therefore, copper iodide and sodium carbonate solutions followed by UV-irradiation were used to detect the pollutants as bright fluorescent spots. This method did not pose the difficulties encountered in the previous method. Since no work of this type has yet been done on Tin(IV) molybdosilicate papers, however, this technique has been employed only on the simple papers. Hence, we have chosen to employ the technique on the papers impregnated with Tin(IV) molybdosilicate. Now, we conclude that solvent extraction using chloroform coupled with fluorescent detection can be used as the reliable technique for the monitoring of the biocides containing tertiary nitrogen in any water sample.

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CHAPTER-V

CHAPTER - V

PREPARATION AND X-RAY DIFFRACTION STUDIES OF THE ION EXCHANGE BEHAVIOUR OF THE SYNTHETIC CRYSTALLINE SILICOMOLYBDIC ACID

The use of the heteropoly acid salts as inorganic ion exchangers is of recent origin. Smit et al.[1] studied the ammonium salts of several 12-heteropolyacids and arrived at some general conclusions. These substances show greater selectivity among neighbouring members than the zirconium phosphate type materials.

Heteropoly acids[2,3] have been used for the detection of proteins, amino acids, uric acids, phenols and sugars. A few of them in the presence of ruthenium(IV) and iridium(IV) chloride complexes have been used for the oxidation of saturated hydrocarbons and as catalytic reagents in other organic syntheses. They possess a remarkable potentiality in the dye industries.

The ammonium salt of 12-tungstophosphoric acid was prepared by the method of Wu[2], while ammonium 12-tungstoborate was prepared by the method of Signer and Gross[4]. The other ammonium salts were obtained by the method of Illingworth and Keggin[3] and the free acids as described in "Inorganic Syntheses" by H.S. Booth[5].

Silicomolybdic acid has been prepared by P.Parravatier[6] as hydrosilicododecamolybdic acid, $(SiO_2.4H_2O)\ 12MoO_3.22H_2O$ by the

action of dilute hydrochloric acid on octomercurous silicododecamolybdate, $H_8[Si(Mo_2O_7)_6]$. Smith[6] obtained crystals of hydrosilicododecamolybdic acid, $(2H_2O.SiO_2).12MoO_3.30H_2O$ by adding tetrasodium silicododecamolybdate, $2Na_2O.SiO_2.12MoO_3.21H_2O$ in cold to a large excess of dilute sulphuric acid (1:5).

Silicomolybdic acid and its ammonium salts were first prepared by Keggin[7]. According to Keggin in the case of 12-tungstophosphoric acid, $H_3(PW_{12}O_{40})$ the structure of the anions consists of a PO_4^{3-} tetrahedron surrounded by $12WO_6$ octahedra as a shell, together by shared oxygen atoms. The best form of expression is $H_3[P(W_3O_{10})_4]$ to indicate a modified PO_4^{3-} tetrahedral group, in which each of the four oxygen atoms has been replaced by a $W_3O_{10}^{2-}$ group, each $W_3O_{10}^{2-}$ group consisting of three WO_6 octahedra sharing oxygen atoms with other octahedra. It is probable that other heteropolyacids have similar structures[8].

The present report deals with the characterisation of silicomolybdic acid. The ion exchange mechanism for the exchange of the H^+, Li^+, Na^+, K^+ and NH_4^+ ions has been investigated using pH-titration and X-ray diffraction studies of the exchanged phases.

Although, crystalline silicomolybdic acid has been synthesised by many authors as described above, its ion exchange properties have not been studied so far. The results obtained by us in this direction are summarised below.

EXPERIMENTAL

Reagents

Sodium molybdate dihydrate (Veb Jenn Pharm, Germany), Sodium silicate (Riedel De Haen AG, Germany). Other chemicals and reagents used were BDH (England) analar or A.R. grade.

Instrumentation

UV-VIS/4 (HACH) spectrophotometer and Spekol (GDR) for colorimetric determinations, thermobalance for T.G.A., Chromel-aluminal thermocouple for D.T.A., muffle furnace for heat treatment, spectromom-2000 for F.T.I.R. spectra, Philips PW-1060 X-ray unit for X-ray diffractograms and Misco model L_1-102 pH-meter for pH measurements were used.

Synthesis of silicomolybdic acid

Silicomolybdic acid has been synthesized by the method of Harold Simmons Booth[5] which is described as follows:

50 g of sodium molybdate was dissolved in 200 ml of water, and the solution was heated to 60°C. To this solution was added 20 ml of concentrated HCl (density 1.18). The mixture was stirred vigorously with a motor stirrer while 5 g of sodium silicate

(density 1.375) dissolved in 50 ml of water was added. While the stirring was continued, 60 ml of concentrated HCl was added dropwise from a separatory funnel. The slight precipitate of silicic acid was filtered off through a glass wool asbestos filter. The filtrate was cooled and extracted with a slight excess of ether.

The solution and the ether formed an emulsion very rapidly; consequently they should be shaken together rather gently, preferably with a rotary motion. The ether complex was diluted with one-half of its volume of water, and the ether rapidly displaced by a stream of air. Should the solution become green, the yellow colour can be restored by adding a little concentrated HNO_3.

For purification the product was dissolved in a mixture of 50 ml of water and 15 ml of concentrated HCl and extracted again with ether. The ether was removed as before, and the yellow liquid was concentrated at 40°C. It was finally crystallised at room temperature. Care must be taken to guard against reduction by dust particles. A little concentrated HNO_3 would reoxidise the acid and restore the yellow colour.

The crystals thus formed contain about 29 molecules of water of hydration. Most of this water could be removed by heating the acid at 40°C for 3 to 4 days or drying in a desiccator. The product then contains 5 or 6 molecules of water. The general formula of silicomolybdic acid is $H_4SiMo_{12}O_{40} \cdot x\,H_2O$.

Ion Exchange Capacity

The ion exchange capacity of Silicomolybdic acid was determined for various cations by the colum elution method[9]. The results are given in Table 13.

Chemical Stability

200 mg of Silicomolybdic acid was kept for 24 hours in the concerned acid solutions with intermittent shaking. The undissolved material was removed. Silicon and molybdenum were determined by the heteropoly blue method[10] using Bausch & Lomb Spectronic 20 spectrophotometer at 700mμ and the acetone method[11] at 420 mμ, respectively. The results are presented in Table 14.

Thermogravimetric analysis (T.G.A.)

The T.G.A. was performed in a thermobalance with the heating rate of 10°C/min. The results are plotted in Figure 7.

Differential Thermal analysis (D.T.A.)

The D.T.A. was recorded in the atmosphere of N_2 using chromel-aluminal thermocouple at the heating rate of 12.5°C/min. The results are shown in Figure 7.

TABLE - 13

Ion Exchange capacity of Silicomolybdic acid for various cations

S.No.	Ion	Ionic Radii (Å)	Hydrated ionic Radii (Å)	Ion Exchange capacity (meq/g)	Corresponding Ionic form 1st "d" spacing (Å)
1.	H^+	-	2.82	0.70	3.50
2.	Li^+	0.60	3.82	0.75	3.87
3.	Na^+	0.95	3.58	0.78	3.89
4.	K^+	1.33	3.31	0.80	4.02
5.	NH_4^+	1.48	3.31	0.76	4.24
6.	Mg^{2+}	0.65	4.28	0.70	-
7.	Ca^{2+}	0.99	4.12	0.72	-
8.	Sr^{2+}	1.13	4.12	0.74	-
9.	Ba^{2+}	1.35	4.04	0.76	-

Table - 14

Chemical Stability of Silicomolybdic Acid in different solvents

S.No.	Solvents	Silicomolybdic Acid	
		Silicon (mg/50 ml)	Molybdenum (mg/50 ml)
1.	4N HCl	0.065	135
2.	4N H_2SO_4	0.040	25
3.	4N HNO_3	0.030	15

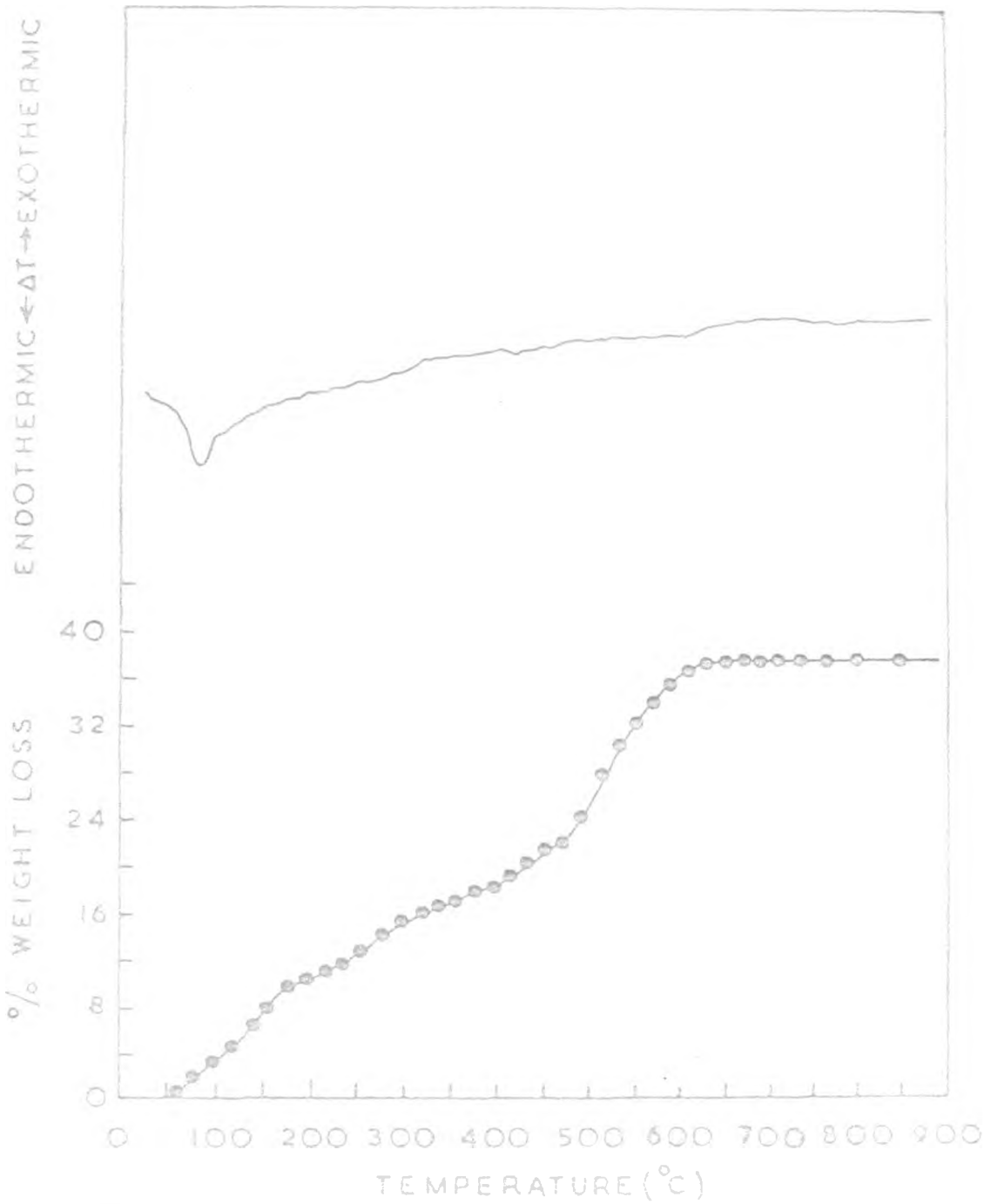


Fig. 7 T.G.A and D.T.A. curves of Silicomolybdic acid

[illegible]

Silicomolybdic acid was heated in the muffle furnace at different temperatures for 1 hour. The effect of heat on its ion exchange capacity is shown in Table 15.

I.R. Studies

The I.R. spectra of silicomolybdic acid at various temperatures were taken by the KBr disc technique and the results are shown in Figure 8.

[illegible]

a. [illegible]

The bed of 1 g ion exchanger in the H^+ form was prepared in the standard ion exchange column through which 0.1M metal chloride solution was passed at the flow rate of 1 ml/min. When the pH of the effluent was identical to that of the eluent, the H^+ ions liberated by the exchanger were estimated by titration against the standard sodium hydroxide solution.

b. [illegible]

Each point in the titration curves was obtained by equilibrating (under constant shaking). 200 mg of the ion exchanger with 0.01M solution of [illegible] and [illegible] (Mercetal) in forward titrations and

TABLE - 15

Heat treatment of Silicomolybdic Acid in the $H^{\oplus}$ form

S.No.	Temperature (^{o}C)	Weight of the Exchanger taken (g)	Weight of the Exchanger found (g)	Ion Exchange Capacity(meq/g)
1.	40	1.5000	1.5000	0.80
2.	100	1.5000	1.4500	0.82
3.	200	1.5000	1.3850	0.83
4.	400	1.5000	1.2600	1.53
5.	600	1.5000	1.2550	1.67
6.	800	1.5000	1.2400	1.78

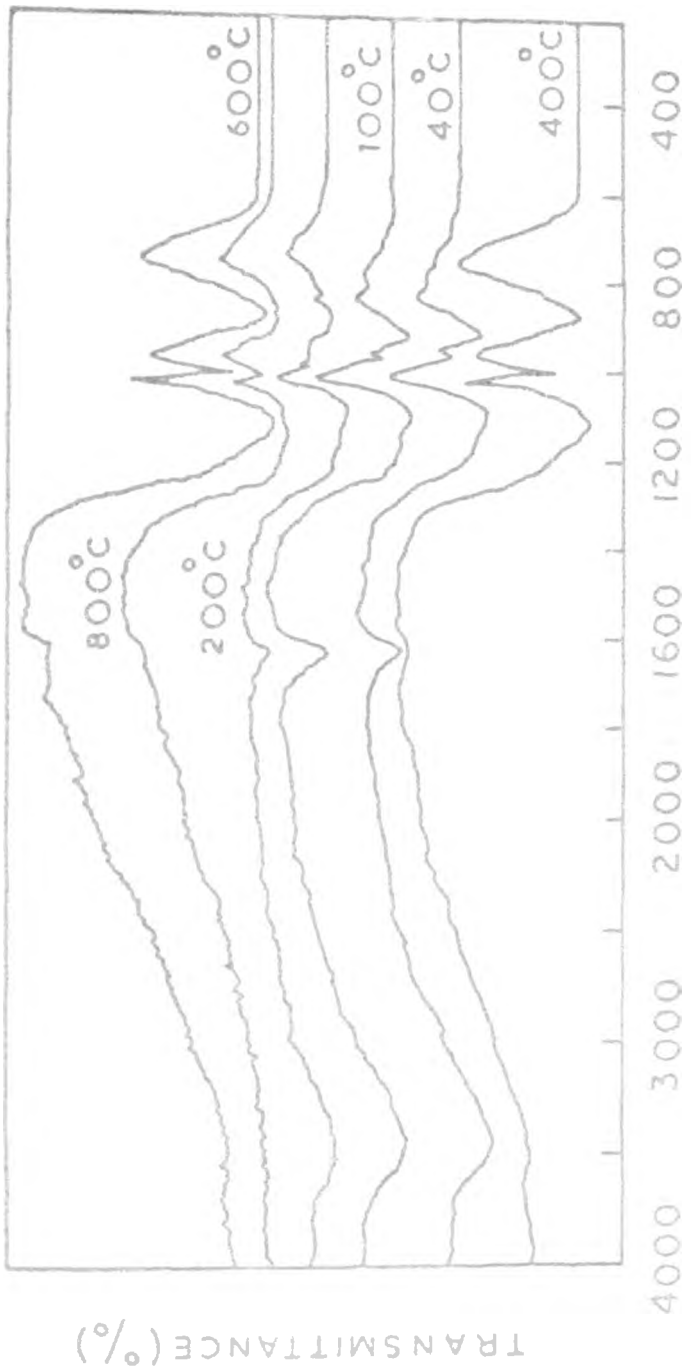


Fig. 8 I R Spectra of Silicomolybdic acid dried at different temperatures

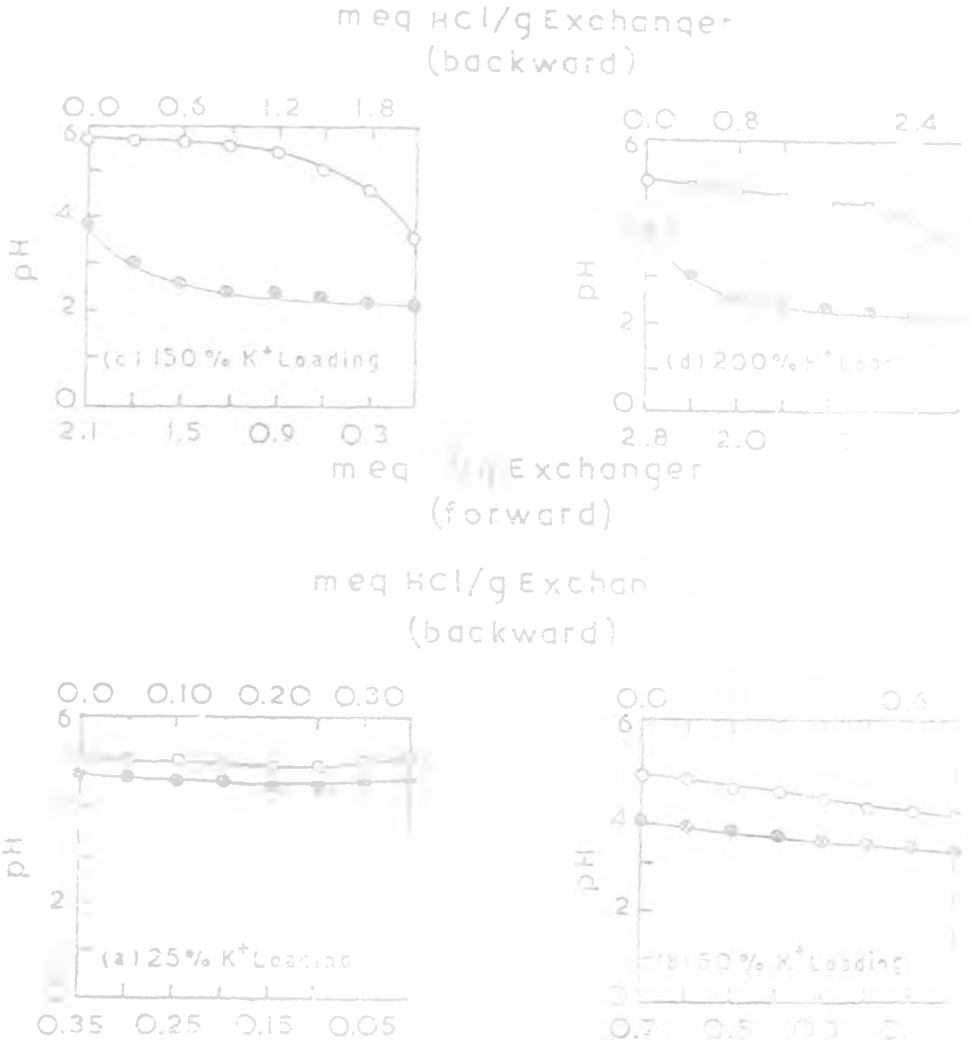
NaOH and HCl for backward titrations. The quantities of solutions taken for the equilibrium were according to their percent loadings. The ionic strength was kept constant for a set of a particular percent loading. The shaking was carried out at room temperature. After the equilibrium attainment the pH of the supernatant solutions was measured. The curves of the titration results for different percent loadings are plotted in Figures 9 and 10.

X-ray Diffraction Studies

Different ionic forms of silicomolybdic acid were prepared by equilibrating its H^+ form with 0.1M of the respective metal chloride solutions. These were filtered and washed several times with demineralised water. These were dried in an electric oven at 40°C. The X-ray diffraction pattern of all ionic forms (i.e. H^+, Li^+, Na^+, K^+ and NH_4^+) were recorded by Philips PW-1060 X-ray unit using nickel CuK_α radiations. The calculated "d" spacings and relative intensities are given in Table 16.

RESULTS AND DISCUSSION

The ion exchange capacities in the various ionic forms, the ionic radii and the hydrated ionic radii[12] of the ions used are given in Table 13. The ion exchange capacity in the various forms is in the following order:



pH-Titration curve
$K^+ \rightleftharpoons H^+$ with different percentiles

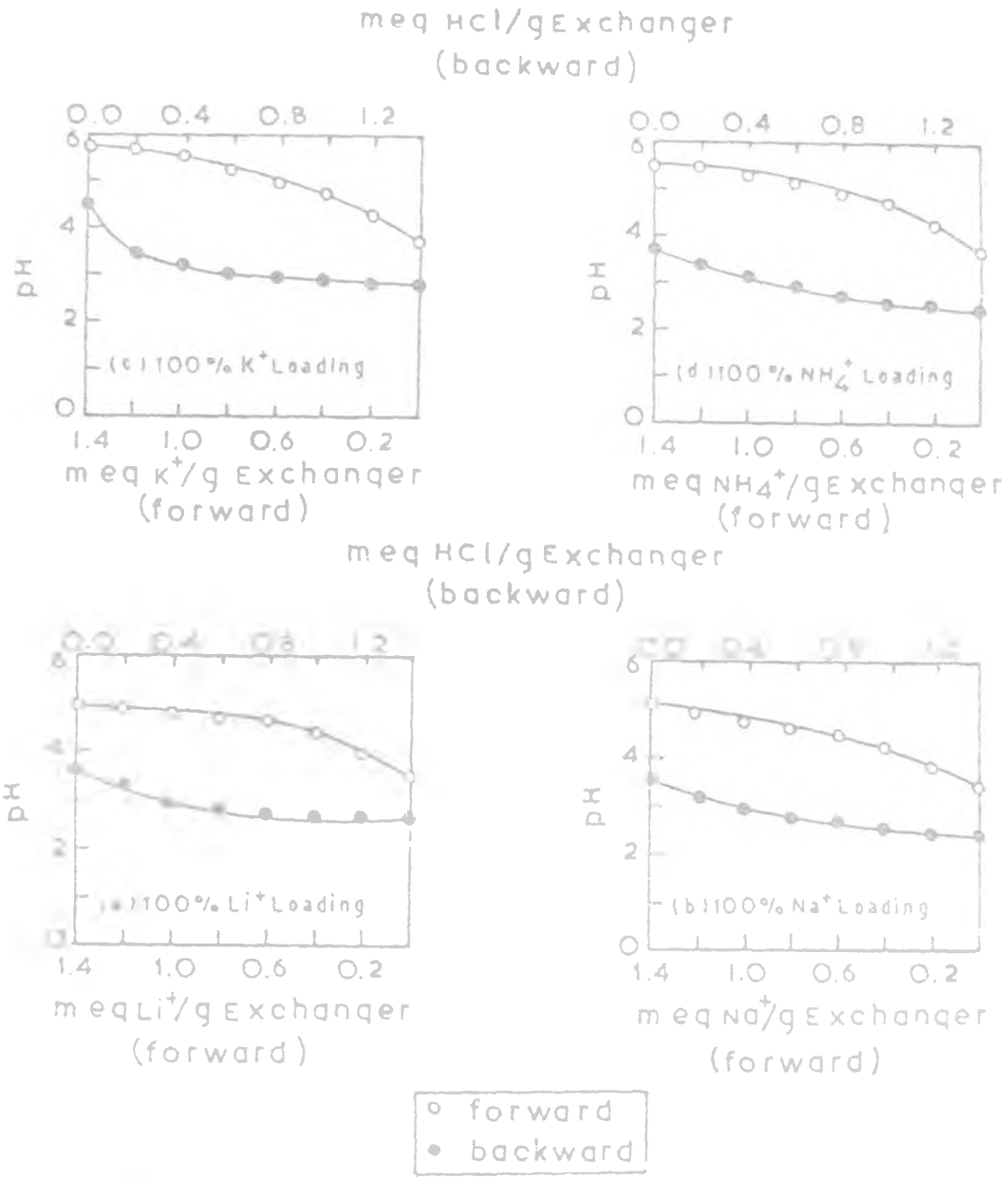


Fig. 10 pH-Titration curves with 100 % loadings for various cation exchanges.

Table - 16

"d" spacings and relative intensities of the H^+, Li^+, Na^+, K^+ and NH_4^+ forms of silicomolybdic acid

S.No.	H^+ form		Li^+ form		Na^+ form		K^+ form		NH_4^+ form	
	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
1.	3.50	100.00	3.87	20.80	3.89	22.53	4.02	15.86	4.24	8.15
2.	3.47	80.49	3.49	100.00	3.50	100.00	3.85	18.62	3.99	8.15
3.	3.06	70.80	3.47	100.00	3.47	85.09	3.62	100.00	3.86	19.87
4.	2.90	21.24	3.06	72.11	3.06	71.12	3.06	5.24	3.48	100.00
5.	2.55	46.90	2.90	26.92	2.91	22.53	2.99	16.55	3.39	10.87
6.	2.16	9.93	2.66	27.88	2.67	25.94	2.94	18.62	3.06	56.52
7.	2.12	16.81	2.54	52.88	2.55	52.40	2.90	15.17	2.90	11.95
8.	2.01	25.66	2.16	17.30	2.16	15.49	2.85	16.55	2.65	11.41
9.	1.96	18.58	2.01	25.07	2.11	21.12	2.55	41.37	2.54	38.04
10.	1.87	24.78	1.96	35.57	2.01	30.99	2.21	10.34	2.16	4.34
11.	1.86	22.12	1.86	24.04	1.96	22.53	2.11	15.86	2.11	11.41
12.	1.64	24.78	1.83	27.88	1.86	26.76	2.01	23.45	2.00	20.65

(Table - 16 contd.)

Sl. No.	H^+ form		La^+ form		Na^+ form		K^+ form		NH_4^+ form	
	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
13.	1.60	15.92	1.82	19.23	1.84	14.08	1.97	6.20	1.95	12.50
14.	1.58	12.39	1.77	16.34	1.82	12.67	1.95	14.48	1.86	13.04
15.	1.50	7.96	1.74	15.46	1.77	10.56	1.86	17.24	1.84	4.34
16.	1.39	7.07	1.72	14.47	1.74	11.26	1.83	10.34	1.85	5.97
17.	-	-	1.64	22.11	1.72	11.28	1.76	5.52	1.76	1.63
18.	-	-	1.60	29.80	1.65	17.60	1.73	6.09	1.73	2.71
19.	-	-	1.57	22.11	1.64	28.17	1.67	22.76	1.64	20.10
20.	-	-	1.39	16.34	1.60	20.47	1.59	12.41	1.59	4.35
21.	-	-	-	-	1.40	10.56	1.57	8.27	1.39	4.39
22.	-	-	-	-	1.39	11.97	1.56	4.13	1.56	8.15
23.	-	-	-	-	1.36	16.10	1.36	10.34	-	-

$$Cs^+ > Na^+ > NH_4^+ > Li^+ > K^+$$

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

Thus the exchanger shows a preferential uptake for the K^+ and Ba^{2+} ions.

The chemical stability (Table 14) shows that the material is fairly stable in 4M nitric acid and sulphuric acid but it dissolves significantly in 4M hydrochloric acid probably due to the high solubility of silicon tetrachloride.

A peculiar behaviour of this material is that the ion exchange capacity increases with increase in the drying temperature. The ion exchange capacity up to 200°C remains constant. However, when the drying temperature is further increased above 400°C, a rapid increase in its ion exchange capacity is observed (Table 15).

The thermogram of silicomolybdic acid (Figure 7) shows a continuous loss in weight above 100°C. When the temperature is increased above 500°C the weight loss is rapid and continues up to 600°C after which the weight becomes constant. The loss in weight up to 500°C (24%) may be due to the loss of external water molecules (as evident from I.R. spectra). The general formula of silicomolybdic acid given by H.B. Booth[5] is $H_4SiMo_{12}O_{40}\cdot nH_2O$. It appears that the formula of acid is $H_4SiMo_{12}O_{40}\cdot 32H_2O$ as the number of water molecules calculated from the formula given by Alberti[13] is 32.

Alberti's formula is given as,

$$18n = \frac{X(M+18n)}{100}$$

where, X is the % weight loss at a particular temperature;
M is the molecular weight of the material and
n is the number of external water molecules

The pH-titration curve has only one inflection point showing that only one type of H^+ ions are present. If Zn^+ ions are exchanged the ion exchange capacity at room temperature is 0.82 meq/g as calculated from the Alberti's formula. This value is very close to the experimental value (0.80 meq/g at room temperature). The weight loss above 100°C is due to the loss of external water molecules. This process continues and again if it is supposed that all the external water molecules are lost above 600°C (as is evident from the I.R. spectra that the peak at 3500 cm^{-1} and 1650 cm^{-1} are due to the loss of water molecules) then the ion exchange capacity should be due to only $H_4SiMo_{12}O_{40}$ and no water molecule. The ion exchange capacity calculated from the Alberti's formula is found to be 1.0 meq/g. However, the experimental value is found to be 1.67 meq/g at 600°C. It shows that the experimental value is much higher than the calculated value. If we assume that Zn^+ ions instead of Zn^+ ions are exchanged at 600°C the calculated ion exchange capacity at 600°C is found to be 1.62 meq/g which is close to that of the experimental value (1.67 meq/g at 600°C).

The D.T.A. curve (Figure 7) shows only an endothermic peak in this region (around 100°C) which is due to dehydration. It is also confirmed by the weight loss. However, after 600°C the weight loss becomes constant.

The I.R. spectra of silicomolybdic acid dried at 40°C (Figure 8) show five strong peaks at about 3500 cm^{-1}, 1600 cm^{-1}, 1100 cm^{-1}, 960 cm^{-1} and 900 cm^{-1}. The broad peak at 3500 cm^{-1} may be due to the presence of external water molecules and the hydroxyl groups[14, 15]. The second sharp peak at about 1600 cm^{-1} may be attributed to water molecules. The third peak at 960 cm^{-1} is due to the molybdenum-oxygen bond. The fourth peak at 960 cm^{-1} is due to the silicon compound and fifth or the last peak at 900 cm^{-1} may be due to the molybdate ion[8].

The I.R. spectra of silicomolybdic acid dried up to 400°C (Figure 8) do not show any change. However, above 600°C the peaks due to water molecules are lost.

The X-ray diffraction analysis results (Table 16) show that the H^+ form of silicomolybdic acid exhibits the first "d" spacing value of 3.50 Å. After being exchanged with alkali metal ions there is a continuous increase in the "d" spacings. The first "d" spacing becomes 3.87 Å in the Li^+ form, 3.89 Å in the Na^+ form, 4.02 Å in the K^+ form and 4.24 Å in the NH_4^+ form. As the Li^+ ion has the smallest ionic radius hence the "d" spacing is the least in this case showing that the ion exchange occurs in the dehydrated form. The hydrated Li^+ ion has a larger radius and so

it gives rise to a lower ion exchange capacity.

pH-titration curves for $K^+ \rightleftharpoons H^+$ of different percent loadings are shown in Figure 9 and those of 100% loadings of Li^+, Na^+, K^+ and NH_4^+ ions are shown in Figure 10.

The hysteresis loop appears in all the curves. The least hysteresity takes place in 25% loading. It shows that up to 25% exchange the reaction is reversible and later on it becomes irreversible due to phase transition.

The appearance of the "d" lines in the X-ray diffractograms is in the following sequence:

$$K^+ > Na^+ > NH_4^+ > Li^+ > H^+$$

This may be explained as follows:

The exchange occure in the dehydrated form of the cations hence as the K^+ ion is the least hydrated of the ions considered here the K^+ ion exchange takes place most easily. This fact is also supported with the highest ion exchange capacity of the K^+ form of silicomolybdic acid (Table 13). It is probably for this reason that the K^+ ion is coprecipitated whenever direct precipitation of ammonium salts of heteropoly acids is performed[16].

Due to considerable changes in the "d" spacings of the Li^+, Na^+, K^+ and NH_4^+ forms with H^+ form these changes show that the exchangeable H^+ ions are interlayerly bonded. This causes changes in the X-ray diffraction patterns of the different ionic forms. The pH-titration curves reveal that two types of exchange behaviour

take place. At lower percent loadings, i.e. at 25% loading no remarkable hysteresity appears but it increases on increasing the percent loading. It shows that the crowding in the lattice of silicomolybdic acid begins at greater than 25% loadings as the lattice becomes progressively less stable to hydrolysis with the Li^+, Na^+, K^+ and NH_4^+ ions in higher loadings. The less stability towards hydrolysis causes the formation of more new phases and the occurrence of sizable hysteresis loop.

In view of this study it may be concluded that the ion exchange in silicomolybdic acid takes place with phase transition.

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SUMMARY

ABSTRACT

The "Studies on the synthetic inorganic ion exchangers based on heteropoly acids and their salts" are described in the present thesis. It is mainly based on the synthesis and ion exchange properties of Silicomolybdic acid (an heteropoly acid) and Tin(IV) molybdosilicate (an heteropoly acid salt). The thesis consists of five chapters.

The first chapter is introductory and discusses briefly about the fundamentals of the ion exchange process and the ion exchange materials. Heteropoly acids, their salts and their important analytical applications are described in some detail. The previous work done on heteropoly acids and their salts has also been reviewed thoroughly in this very chapter.

The second chapter deals with the synthesis and ion exchange properties of Tin(IV) molybdosilicate. Many Tin(IV) molybdosilicate samples have been synthesised under different conditions. The most stable sample shows an ion exchange capacity of 0.65 meq/g in the H^+ form at 40°C. Its ion exchange properties were studied with the help of pH-titrations, I.R. and X-ray spectroscopy, thermogravimetric analysis and the differential thermal analysis. Tin(IV) molybdosilicate is thermally much more stable than other Tin(IV) based ion exchangers and it shows considerable increase in its ion ex-

change capacity (1.20 meq/g) at 300°C. The adsorption of different metal ions in demineralised water, various concentrations of nitric acid and 0.01M ammonium nitrate has been studied. Tin(IV) molybdosilicate is found to be highly selective for Th(IV). The analytical and industrial importance of this material has been demonstrated by achieving the following eight quantitative binary separations:

$$Ag^{2+} - Mn^{2+};\ Ag^{2+} - Cd^{2+};\ Mn^{2+} - Al^{3+};\ Mn^{2+} - Ni^{2+};$$
$$Mn^{2+} - Zn^{2+};\ Fe^{3+} - Al^{3+};\ Fe^{3+} - Zn^{2+} \text{ and } Fe^{3+} - Cd^{2+}.$$

A comparison of the ion exchange properties of this material has also been made with other Tin(IV) based ion exchangers.

In the third chapter the paper chromatographic behaviour of some organic pollutants (pesticides and texicants) has been studied using Tin(IV) molybdosilicate papers in various organic and inorganic solvents. Several qualitative binary and ternary separations have been achieved which were not possible on plain papers. The method developed can be successfully applied for certain isomeric differentiation.

The fourth chapter is based on a simple extraction fluorescence technique which has been developed for the monitoring of certain organic pollutants containing tertiary nitrogen in water on Tin(IV) molybdosilicate papers. Various organic and inorganic developers have been employed to study the chromatographic behaviour. Saturated solution of copper iodide in acetonitrile, saturated solution of sodium carbonate and UV-light have been used as detectors.

The fifth and the last chapter describes the studies on silicomolybdic acid. The crystalline silicomolybdic acid has been synthesised and characterised through its ion exchange capacity, chemical stability, I.R. spectra, thermogravimetric analysis, differential thermal analysis, and X-ray diffraction pattern. The material shows a unique feature, i.e., its ion exchange capacity increases with increase in the drying temperature from 40°C(0.80 meq/g) to 300°C (1.78 meq/g). The mechanism of ion exchange of monovalent cations has been investigated through potentiometric titrations and X-ray diffractograms of the exchanged phases. It has been found that ion exchange in silicomolybdic acid takes place with phase transitions.